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THE VIRGINIA JOURNAL OF SCIENCE

A JOURNAL ISSUED QUARTERLY BY THE VIRGINIA ACADEMY OF SCIENCE

Vol. 3, New Series | JULY, 1952 | No. 3

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VOL. 3 JULY, 1952 No. 3

THE VIRGINIA JOURNAL OF SCIENCE

PUBLISHED FOUR TIMES A YEAR: IN JANUARY, APRIL, JULY AND SEPTEMBER, BY THE VIRGINIA ACADEMY OF SCIENCE

Printed by the Commonwealth Press, Inc., Radford, Va.

CONTENTS

	Pages
Threads of Geology — ARTHUR BEVAN	153-168
Further Studies on the Production of Bovine Hyperkeratosis by the Administration of a Lubricant — WILSON B. BELL.	169-177
Dissociation and Diffusion of Electrolytes from Clays as Determined by the Donnan Membrane Equilibrium — JOHN D. PENDLETON	178-201
Size Variations and Sexual Dimorphism in a Brood of Common Garter Snakes, *Thamnophis o. ordinatus* (L.) —JOHN THORNTON WOOD AND ROBERT HOLDEN WILKINSON	202-205
The River Shrimp, *Macrobrachium ohione* (Smith), in Virginia —HORTON H. HOBBS, JR. AND WILLIAM H. MASSMANN	206-207
News and Notes	208-217

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Entered as second-class matter January 15, 1950, at the post office at Blacksburg, Virginia, under the Act of March 3, 1879. Subscription— $8.00 per volume. Published at Blacksburg, Va.

Mailed August 25, 1952

THE VIRGINIA JOURNAL OF SCIENCE

VOL. 3, NEW SERIES JULY, 1952 No. 3

THREADS OF GEOLOGY

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"He who sees things grow from the beginning will have the best view of them." *Aristotle.*
"The present is the key to the past." *Hutton.*
"The texture of modern science is the result of the interweaving of the fruitful concepts." *Conant.*

Landscape features can scarcely have meant more to early man than a background in the daily struggle for existence. Hills and valleys, plains and mountains, rivers and lakes engendered neither purposeful reflection nor meditation as to their character, relationships, origin, or environmental effects.

Millenia passed; races evolved and disappeared. Intelligent man began to use stones for crude weapons and tools. He came gradually to recognize local concentrations of flint. Nomadic living no doubt brought other types of rocks and minerals to his fleeting attention.

Rudimentary civilizations slowly evolved. Racial progress came to depend more and more upon the character of the accessible geologic materials in a diversity of environments. For countless centuries, nevertheless, man was imperceptive to most geologic processes and phenomena. Those which occasionally puzzled or terrified him had no significance. Intellectual curiosity did not yet stir him to logical speculations about earth materials or their relations to natural phenomena. He had not become intellectually equipped or sufficiently motivated to ponder upon his geologic environment.

Man with the mental faculties of *Homo sapiens* became dominant upon part of the earth in late Pleistocene time, some 25,000 to 50,000 years ago. Continental ice sheets over the northern half of Europe waxed and waned, and in so doing sharpened man's response to his physical surroundings. The fabric of civilization began to be woven of many strands—material, intellectual and spiritual. Intellect and spirit were within man himself. The material warp and woof were derived from the bounteous heritage of eons of physical evolution of

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Editor's Note: We are pleased to present this invited article by Mr. Arthur Bevan, Past President of the Virginia Academy of Science, and formerly State Geologist of Virginia.

the earth. This physical heritage in all its diversity and complexity is the core of modern geology.

In various stages of early cultural development, sapient man made deliberate use of additional geologic materials. Cro-Magnon man used mineral pigments to record his observations in the remarkable polychromes on cave walls in France. Flint quarries were opened in deposits most suitable for the skillful fashioning of specialized types of tools and weapons. Clays were used for modeling and the making of crude pottery, in the slowly developing ceramic arts. Stones were used for the milling of wild or domesticated grains. Men of the New Stone Age became adept in a primitive manner in the use of earth materials close at hand. But the culturally most revolutionary step forward, the discovery and use of metals, yet lay some 5,000 to 10,000 years in the future. Stone and a few nonmetallic minerals were the essential and dominant geologic materials used by man during his Paleolithic and Neolithic evolution, a span perhaps of a hundred millenia.

The early production of usable metals from ore minerals is hidden among the obscurities of prehistoric centuries. Gleaming fragments of native gold and copper may have been observed in streams where late Neolithic man fished or traveled in his dugouts, or among the sands of lake shores where he constructed his pile villages. Growing curiosity and experimentation led to the production of ornamental and useful pieces of metal. When ore erratics or veins of suitable metals were found, man could begin to develop the art of metallurgy, for fire had long since been his servant. Gold, copper, silver, tin and iron became of increasing importance.

Gemstones were discovered in due course; possibly accidentally among alluvial sands and gravels but also as accessories to ore minerals. They were probably worn first as amulets; later as ornaments. By historic times gems had become one of man's most prized and alluring geologic resources. They became one of the coins of ancient, as well as of modern, commerce.

With the increasing discovery of ore minerals and practical improvements in the reduction of metals from them, man made relatively rapid progress into the dawn period of the historic era. Copper is thought to have been known at least 100 centuries B. C., possibly twice as long, and it was in use certainly 5000 to 4000 B. C. Native gold may have been used even earlier than copper. Man entered the "Bronze Age" of culture by learning how to alloy copper and tin. Its dawn may have been 4000 to 3000 years B. C.; the records of its early principal use lie between 2500 and 1000 B. C. Transition was then made into the dominant "Iron Age," in which the remarkable geologic discoveries and technologic developments have conditioned the material progress of man to the present.

Man has been led into modern culture through the accelerative discoveries and applications of science during the past few centuries. Although some geologic resources were purposively used by man in remote prehistoric times, comprehension and utilization of the facts and principles of geology lagged far behind other cultural attainments. Hence the initial fabric of geology was woven irregularly and sporadically of threads of many lengths and textures. In tracing the evolution of geologic thought, as of any other science, it must be understood that all science is the product of yesterday in the long cycles of intelligent man. But in a short span it has become a primary concern of man and to world civilizations.

Some modern geologic concepts had ephemeral germination among ancient historic cultures in the minds of those endowed with unusual acumen. Pythagoras, for example, in the 6th century B. C., recognized the carving of valleys by streams, the depositional tying of former islands to the mainland, and sea invasions whereby marine shells were left far inland. But in general the intellectual climate and interests were not conductive to the nurture of fundamental concepts of natural science. Uncoordinated observations about common earth features and phenomena were not woven into a definite fabric until the latter part of the 18th century. Part of the long delay in gathering loose ends together was due to the stagnation in the Dark Ages and part to the necessity of first establishing some of the basic principles of the sciences which underlie geology. Even yet, with the spate of discoveries and achievements in all the natural sciences, the fabric of science is being loomed.

Rudimentary geologic observations were first used in practical applications and not for spinning theories. Empirical use through centuries gradually built foundations for interpretations which after some testing became woven into the fabric of geology. The earliest threads in the fabric were spun mainly from the substance of mining geology, embryonic mineralogy and petrology, and economic geology.

Mining geology.—Mining was the first application of geology. We know that Neolithic man, and perhaps some of his ancestors, mined flint. Crude mining of placer gold may have followed. Copper ores were mined some 50 centuries B. C. and tin ores about 25 centuries B. C. Iron was mined in Egypt and Mesopotamia about 1500 B. C. Much of the early mining, however, made only crude use of the principles of economic geology. Some tactics of modern mining geology were employed in some of the extensive and still accessible ancient mines. A trained observer concludes that "the economic geology of those times, though empirical, was certainly well developed, and extreme skill and care were used in studying the local geological conditions." He explains the paucity of information about mines and mining methods on the basis that the miners and "geologists" were slaves and thus beneath the notice of either historian or philosopher. Moreover, industrial pursuits were

ignored by groups primarily interested in art, literature, and philosophy. The secrets of the industrial arts also were jealously guarded.

A most important contribution was made, after the long period of stagnation, early in the 16th century. Agricola, a highly educated and learned physician in Bohemia, was a methodical investigator of mines, ores, minerals and matallurgical processes. His spare-time efforts were given for a quarter of a century to the preparation of a treatise entitled *De Re Metallica,* which described and organized most of the developments in mining geology and incorporated much new material. Published in 1555, shortly after his death, it became a guide to mining men and spurred the winning and treatment of ores. This significant but forgotten treatise was translated into English by Mr. and Mrs. Herbert Hoover, first published in 1912 and reprinted in 1950. The Hoovers state that the clarity of Agricola's contributions is "as crystal to mud in comparison to those of his predecessors and to most of his successors for over 200 years." This professional evaluation applies to Agricola's research in mineralogy and to that part of the field now known as economic geology as well as to mining and metallurgy.

The techniques of mining geology and mining engineering, coupled with fundamental research in the relations and origin of ore deposits, have developed greatly since Agricola's time, especially during the past half century, in meeting the demands of a rapidly expanding industrial economy, gravely burdened with the large-scale loss of irreplaceable mineral resources in two enormously destructive world wars. These advances have been accomplished in large measure through the knowledge and ingenuity of mining men, mineralogists, economic geologists and metallurgists.

Mineralogy.—Mineralogy has been said to be the oldest science and the mother of all geological science. Colorful minerals, striking crystals, and gemstones had attracted men in very ancient times. Mineralogy was probably the first scientific subject to be taught in universities. The early activities either were not recorded or the records have been lost. Preserved is the fact that a pupil of Aristotle (Theophrastus) described 16 minerals and wrote a "Book of Stones." The elder Pliny named several minerals. The general state of early mineralogy is indicated by the fact that fossils were also considered to be minerals.

In the early part of the 16th century, Agricola added 20 minerals to the small list of identified ones and recognized that many more were undescribed and unnamed (some 2000 are now known). His *De Natura Fossilium,* in four parts, was the first serious attempt at a treatise on systematic mineralogy. He, also, did not discriminate sharply between minerals and fossils. He gave the first critical description of crystals and the physical propetise of some minerals. Unlike the fanciful speculations of most of his predecessors, his conclusions were founded upon

systematic, purposeful observations; thus he helped lay the foundation for a branch of geology.

The development of mineralogy during the next two and a half centuries was chiefly of a routine nature—more minerals found, described and named. Significant advances in concepts, in study techniques, and in interpretations were few. Scant growth was made until the 19th and 20th centuries. Many of the laws of crystal symmetry were conceived prior to 1800. The appointment of Silliman in 1802 as professor of chemistry and mineralogy at Yale College gave strong stimulus to the broadening and deepening of research in mineralogy. Further impetus was given by the acquisition of the famous Gibbs collection of 20,000 foreign specimens for display at Yale. Many mineralogic articles soon appeared in the *American Journal of Science,* founded in 1818 by Silliman. In 1837 was published the first comprehensive reference work in English, "The System of Mineralogy," by the young and brilliant mineralogist and geologist, J. D. Dana. Its enduring worth is attested by the fact that the seventh revised edition is now being published. In the third edition (1850) Dana based his classification on a new concept —that minerals are chemical compounds whose formation in the earth's crust obeyed chemical laws and thus had been responsive to their chemical environments. Henceforth, mineralogy was transformed from a descriptive study to analytical research. As Willis stated: "Dead mineralogy came to life." Dana's attitude toward scientific truth—"not to change with the advance of science . . . . is persistence in error"—not only made revised editions of the "System" indispensable, but it reflected a new outlook upon research and changing concepts in geological science.

With the rapid progress of research in chemistry, much attention was given in the 19th century to the composition of minerals. Speculation on crystal form and structure and mineral genesis became increasingly fruitful, and research in the entire field became more balanced. Students of optical mineralogy, aided by new tools, soon made notable contributions to concepts and techniques.

It is astonishing now to recall that at the turn of the century many mineralogists thought that research in their field had almost ended. "All of the commoner minerals had certainly been discovered and exhaustively studied. Little apparently was left that could be added to our knowledge of them." In illuminating contrast stands the brilliant work of 20th-century mineralogists, chemists, and physicists on crystals and minerals. Among the outstanding concepts may be mentioned (1) the atomic structure of crystals; (2) the structure of space-lattices and the exchange of ions; (3) the nature of clay minerals and their relations to geologic and engineering problems; and (4) procedures for the laboratory synthesis of pure minerals and crystals, including gems. These

products of modern research have resulted from new concepts tested and established by evolving chemical and physical research tools and techniques, such as spectrogaphy, radioactivity, X-ray analysis, and differential thermal analysis. Even yet, in the words of a noted mineralogist, the "day is not in sight" when "the science of mineralogy is complete and has become a discipline."

Petrology.—Petrology, the science of rocks, treats of the character, geologic relations, occurrence and origin of rocks, that is, their geologic history. More or less unrelated facts about rocks were recognized by the philosophers and "naturalists" of Arabia, Egypt and Greece. Until the early part of the 19th century the megascopic study of rocks was generally associated with mineralogy and stratigraphy. Ford states in 1918 that "Only within the past fifty years has the systematic investigation of rocks—their composition, relations, and origins—reached a stage that justified the recognition of a distinct branch of science." The abortive attempt of Linnaeus, the botanist, to classify rocks as well as plants on a binomial basis is of historic significance as a reflection of concepts of the middle 18th century.

A historic controversy of wide and deep significance arose during the 18th century from scientific interest in the meaning of rocks. The Germanic Neptunists argued with more fervor than objectivity that all rocks—even igneous rocks—were chemical precipitates from oceanic waters. This dogma was finally controverted by the exact and thorough field studies of the British Plutonists, who proved the true origin of igneous rocks. The debate had numerous repercussions, particularly upon theories concerning the origin of ore deposits.

Petrogaphic research—the systematic megascopic and microscopic description of rocks—was aided greatly by the discovery and use of new techniques. Two epochal treatises on rocks appeared during the 1820s, one in France and the other in Germany. According to Cross, they placed "the classification of rocks upon a firm basis as a systematic science." A strategic concept of these petrographers was that the characters of rocks and their geologic environments were genetically related and thus should be determinative factors in scientific classifications. As stated in 1876 by the renowned Rosenbusch, "A rock becomes alive to me only when I have grasped its relations to our planet and its history." Petrographic research advanced steadily when mineralogists and chemists joined efforts in the determination of the actual components of rocks and their relationships.

Petrologists for a long time focused research on igneous rocks, which had originated in almost bewildering diversity in manifold geologic environments from molten masses deep within the earth's crust. This partiality was due to the fascinating assemblages of minerals and the principles of mineral genesis involved, the genetic history of diverse rock

types, and the apparent relations of ore deposits to many igneous rocks. The complex metamorphic rocks, derived by alteration in changing geologic environments, next received detailed study as research techniques and concepts were developed in the late 19th century and the early 20th century. The widespread, highly significant aggregates of mechanical, organic and chemical particles—the sedimentary rocks—were petrologically long neglected although of increasing interest to stratigraphers and earth historians. The intensive and extensive explorations during the last third of a century for petroleum, natural gas, groundwater and industrial minerals in these sedimentary host rocks made more thorough petrologic investigations inevitable.

An illustration of the development of research to a peak with consequent tapering off to an apparent plateau is noted in the statement of Gregory about the scientific study of rocks: "By 1850 the possibilities of increase of knowledge through the study of rocks appeared to have been exhausted; no further steps seemed possible . . . .Petrography had come to a blank wall." But it is an inherent characteristic of scientific research that the birth of a new and stimulating concept or the discovery of a new and perhaps revolutionary research technique pushes back the frontiers of that particular science. In petrology, the use in microscopes of the Nichol prism for polarizing light, which was invented in 1828, opened up fields far beyond the "blank wall." Another new technique speeded achievement: grinding an opaque rock in slices so thin (thin sections) that for practical microscopic study they are almost transparent.

Geochemical studies have added greatly to the knowledge of the distribution and migration of elements in the rocks of the earth's crust. Mining and drilling in many parts of the world have unlocked bountiful storehouses of geologic data, much of it of a petrologic character. Mines can now be made more than a mile deep; borings for oil to depths of three to four miles are almost commonplace; deep prospecting by the diamond drill is routine procedure. Geophysical exploration also has resulted in deep reconnaissance studies of the outer shell of the earth.

Economic Geology.—Gold and copper were probably the first ores used by man as he was starting up the material ladder of civilization. Casual use may have been as remote as 200 centuries B. C.

Deliberate search for ore deposits ensued as the usefulness and worth of metals expanded. Mining and processing of copper, tin and iron ores became established industrial arts from about 5000 to 1500 B. C. Until the 16th century of the Christian era, or even later, the practices were primarily empirical without knowledge of the principles of economic geology. There was no science of economic geology until the 18th or 19th centuries.

The early concepts about ores were fantastic. Examples of numer-

ous fruitless interpretations are: (1) Metal-making vapors emanated from a perpetual fire in the interior of the earth; (2) ore veins and veinlets were the branches and twigs of a huge "tree" of metal rooted deeply in the earth; (3) ores were reproduced by "seeds" and grew like plants; and (4) base metals were somehow transmuted into gold. There prevailed also the authoritarian view that all rocks, minerals and ores were original parts of a supernaturally created earth.

The salient facts about ores were long considered to be the core of economic geology; studies of them and theories about their origin long provoked discussion and still stimulate friendly controversy. Agricola spun the first tangible threads of economic geology as he studied mines and minerals in Bohemia. In the introduction to their translation of Agricola's *De Re Metallica,* the Hoovers state: "In his propositions as to the circulation of ground waters, that ore channels are a subsequent creation to the contained [containing] rocks, and that they were filled by deposition from circulating solutions, he enunciated the foundation of our modern theory, and in so doing took a step in advance greater than that of any single authority." Agricola's significant contribution to the embryonic science of geology lies in the fact that his interpretations were based upon both methodical field observation and logical reasoning.

During the next two centuries various facets of ore deposits were explored. Late in the 18th century a heated international controversy began to brew about the genesis of ore veins with two radically divergent concepts as its basis. The Neptunists, led vigorously by the gifted Werner in Germany, dogmatized that ore veins had been formed from oceanic waters which percolated downward in the earth's crust. The opposing Plutonists, with the versatile Hutton in Great Britain as their champion, strongly advocated a magmatic source. They believed that igneous rocks and ores were closely akin and perhaps consanguineous.

The approaches of the two schools to the solution of this absorbing scientific and economically significant problem were in strong and illuminative contrast. The Neptunists were mainly speculative and attempted to fit observed facts to preconceived theory whereas the Plutonists reasoned logically from field observations to a working hypothesis. Hutton and his followers proved the magmatic origin of igneous rocks and the association of many ore deposits with them. The essence of their argument, that many ores were deposited by ascending magmatic vapors and liquids, is widely accepted today. Some difference of opinion exists as to the relative roles of vapors and liquids, depths at which the ores crystallized from the fluids, and the relations of some ore deposits to igneous rocks. A concept prevalent into the 20th century was that meteoric waters circulating in the rocks had played a major role in the concentration of ores.

Field evidence painstakingly gleaned from many mining districts

by numerous economic geologists has caused the magmatic concept to gain wide acceptance over the meteoric concept. The data have been substantiated and supplemented by much geochemical research on ore and rock minerals. However, one should not lose sight of the fact that the diversity of ore deposits and their geologic environments make other origins probable for some of them.

The Industrial Revolution in England in mid-18th century made coal and metals indispensable to a progressive industrial society. Hence for a long time economic geology was essentially a study of ore deposits. During the late 19th and in the 20th century all geologic materials of actual or potential use have come within the purview of economic geology for their economic utilization involves numerous geologic problems. Consequently, increasing interest has developed in the specific geology of petroleum, coal, groundwater, and manifold industrial minerals (nonmetallics) and in conceptual bases for precise research on them. Each of these groups of geologic resources, moreover, has become of critical importance to the American way of life and to our participation in international affairs. Economic geology in the broadest sense has become, therefore, a paramount factor in the continued welfare of our modern society.

Petroleum Geology.—Petroleum geology is a relatively recent phase of economic geology. Oil which had seeped from fissures in the rocks and its residues were recognized and probably used in rather remote antiquity. They had considerable local use in early historic times and during periods recorded in the Bible. Herodotus in the 5th century B. C. recorded the production of asphalt and oil from a well, and rock oil long has had considerable use for medicinal purposes. Oil contaminated some of the salt licks upon which the westward migrants in the Appalachian region depended. In 1806 a well was drilled near Charleston, West Virginia, to obtain salt brine. This idea had far-reaching consequences for the future of the petroleum industry and petroleum geology in North America. The associated oil was a nuisance to seekers of salt brines, but within slightly more than a century economics had so drastically changed that oil was eagerly sought throughout the world.

Oil in "large" quantity was found in a fairly deep well drilled in 1814 in Cumberland County, Kentucky. The pioneer markets could absorb small amounts only for medicinal use, lighting, and lubricants. A salt well drilled in 1847 near Pittsburgh to a depth of more than 400 feet produced oil. This oil and its attempted medicinal use led by an interesting chain of circumstances to the drilling in 1859 of the historic Drake well in northwestern Pennsylvania. "Oil fever" swept the country. In less than 20 years, oil had been discovered in many places from Pennsylvania to California.

The first sites for oil prospecting were naturally the petroliferous

salt licks and wells and areas of oil and gas seepages and residues. Geologists, however, had noted as early as 1844 the association of oil with a definite structural pattern of sedimentary rocks in parts of Canada, and later in Pennsylvania and West Virginia. By 1860 the concept had developed that migrating petroleum had been trapped in inverted basins (anticlines) in sedimentary rocks. This fundamental concept gave strong impetus to the youthful oil industry. In the 1880s it became an established principle of oil prospecting by geologists. Rule-of-thumb drillers ignored or ridiculed the idea, but it has always been one of the guiding concepts of geologic exploration before systematic drilling. In the meantime other essential geologic conditions had been conceived: the presence of a source bed, a porous reservoir rock in the anticline, and an impervious cap rock above the reservoir to prevent the escape of the buoyant oil and gas.

Numerous modifications of the simple anticlinal structure were postulated and tested, and other geologic factors contributory to oil and gas accumulation were observed. Stratigraphic traps—sealed reservoirs within a stratum, e.g., buried coral reefs, beds that wedge out, zones of decreased lateral porosity—have recently received much consideration. The somewhat revolutionary concepts of stratigraphic traps of diverse form, extent, and capacity in turn stimulated much thought and imagination about the fundamental data and principles of stratigraphy and sedimentation, as well as of the characteristics and relations of the voids and the oil-water contacts in the host rocks. Recent studies of the behavior of clay minerals in petroliferous formations bear directly upon the search for oil in particular geologic environments.

The steadily increasing demand for more oil and natural gas has brought forth a train of concepts and new applications of old ones in the whole realm of geologic fundamentals, resulting in "discovery thinking" about geologic environments favorable to commercial oil and gas accumulation throughout the world.

As the geologic characteristics of the concealed reservoirs were discovered, more thought was given to the migration of oil and gas into them. Rise of the more buoyant fluids through water-filled zones in the entrapping anticlines was a generally acceptable explanation. For oil far down the flanks of such folds it was postulated that it had followed water as it receded to lower levels. The latest theory, according to Hubbert, is that oil and gas, together or separately, accumulated in various types of reservoirs as the result of differences in energy potentials of all the fluids occupying voids in the rocks. Many geologic factors, naturally, have affected the amount and site of commercial accumulations. Groundwater in motion in saturated zones has been an impelling factor.

Although much thought has been given by chemists, geologists, and biologists to the origin of petroleum, its exact origin is yet an unsolved

geochemical and biochemical problem. In the latter half of the 19th century, chemists consistently advocated an inorganic origin. They conceived that hydrocarbon compounds had been formed in the earth at high temperatures through the contact of water and gases with alkali metals or with metallic carbides. As recently as 1909 it was stated that "great oil deposits are generated from iron carbides either by or without the agency of water." The concept of inorganic origin was unacceptable to scientists working with the geologic facts.

In this century the organic origin of petroleum and natural gas has become almost axiomatic. As long ago as 1859 Newberry postulated that oil was generated by slow distillation at low temperatures of carbonaceous materials in sedimentary rocks. Others thought that high temperatures in strata undergoing severe deformation, as in the Appalachian orogeny, had been a critical factor. Divergent concepts have been advocated within recent decades as to the relative importance of plant and animal remains as original sources, and stress has been placed upon the role of anerobic bacteria.

Coal Geology.—Coal is another geologic resource that may have been used during remote antiquity. It was mentioned by Aristotle and its use was described by Theophrastus. It had considerable use in the 13th century in England and France, but its general use was restricted by regulations and public disfavor. Coal was discovered in Canada about 1672; it was shipped in 1730, or earlier, from the Richmond Basin in Virginia.

During the nearly two centuries since the Industrial Revolution in England, much attention has been given to technologic improvements in mining, preparation, and use of coal rather than to its geology. Unlike the general use of geology now in the discovery and procurement of petroleum, geology has not been an essential handmaiden to the winning of coal from the earth. Nevertheless, the geology of coal and its geologic relations are becoming steadily of greater importance in the mining and use of coal, and intensive geologic and geochemical research is in progress.

Microscopic study of thin sections and polished surfaces, X-rays, and differential thermal analyses have contributed to an understanding of the geochemical and geophysical characteristics of various coals. Paleobotanical research, e.g. on spores, has given more insight into the geology of coal. The geologic environments of coal, both present and past, have been intensively studied. One objective of these studies has been to formulate satisfactory concepts about the coalification process—the stages from parent vegetation to bituminous coal and anthracite—as of fundamental scientific significance and as an aid to more precise scientific classification of coal.

An early concept postulated that coal was formed *in situ* from

parent plant detritus. The opposing concept was formulated later that the plant debris had been transported to the basins of accumulation, a view which is not generally supported by the geologic evidence. Much thought has been given also to the geologic relations of coal beds and to their repetitive occurrence in a thick sequence of marine sedimentary rocks. Many of the problems have been attacked by intensive study of the paleogeographic and sedimentologic conditions which appear to have favored periodic accumulation of plant debris in extensive swamps near sea level. An interesting and useful recent product of these field studies is the concept of cyclothems-unit sequences of coal-bearing strata cyclically deposited for a long time in certain extensive basins.

Groundwater Geology.—The use of groundwater by man is no doubt as old as the human race. Its geologic environment was longer in being understood than that of most other geologic resources, and even today there is much misunderstanding.

The classical philosophers had fanciful hypotheses about springs, the obvious evidence of large bodies of water underground. Springs were commonly ascribed to the outpourings of huge reservoirs in the earth's interior. Aristotle pointed out that a reservoir as large as the earth itself would be required to furnish all the waters flowing in springs and spring-fed rivers. Hence he concluded that condensation of cold air within the earth's chambers produced the subterranean waters much as atmospheric condensation produced rain.

Other views predominated, particularly under the influence of Biblical dogma. It was thought that springs fed rivers flowing into the ocean from whence water seeped through holes in the ocean floor into subterranean channels which replenished the inexhaustible reservoirs. Some were perplexed by the conversion of saline oceanic waters into the fresh waters of mountain springs. One explanation was that the interior waters were vaporized by the internal fires; the vapors rose through caverns into high mountains to issue as springs.

About the beginning of the Christian era an observant architect deduced that rain and snow falling on mountains seeped into the earth and then moved to springs at the base of mountains. He observed that certain plants are indicators of ground waters. Both concepts are among present hydrologic principles, but he was so far ahead of his time that little credence was given them.

The astute Leonardo da Vinci was an accurate observer of natural phenomena. He appears to have had a modern conception of the hydrologic cycle; rain—groundwater—springs—rivers—water bodies—evaporation—rain. In the middle 16th century a French paleontologist and ceramicist inferred that percolating groundwater followed impervious strata to the spring outlets.

No substantial progress could be made in formulating fundamental

concepts of groundwater geology until at the end of the 18th century observations had been organized into a philosophy at least akin to science. Quantitative data on rainfall, rivers and springs had been obtained during the 17th century. In 1751 the president of the University of Padua in Italy published a book in which he explained in almost modern terms the source of groundwater and the mechanics of its movement. By the middle of the 19th century, according to Meinzer, French scientists had established the "principles of the geologic occurrence of ground water and the hydrostatic theory of artesian flow."

Stratigraphic Geology.—Stratigraphy is concerned primarily with sedimentary rocks — their lithologic characteristics, three-dimensional relationships, fossil contents and geologic history. An important objective of stratigraphic research is the orderly classification of all strata into natural groups, involving all rocks from the oldest to the youngest. It comprises determination of the time sequence and correlation of strata in widely separated regions. Incompletely exposed sections of rocks must be properly fitted into the established time scale, as well as those which are penetrated underground.

Speculations among common rocks in early historic epochs, even until the Renaissance, ranged from the utterly fanciful to conjectures that had germs of scientific truth. Pythagoras, for example, in the 6th century B. C., recognized that seas had inundated the lands and left behind marine shells as witnesses of the invasions. The real geologic significance of fossil shells apparently did not occur to him. Not until the versatile Leonardo da Vinci in the late 15th century studied strata and their fossil contents was it clearly comprehended that those shells are the remains of marine invertebrates that lived in the invading seas.

More interest was aroused by these relics of ancient life than by the drab host rocks. They stimulated and inflamed some of the great controversies about organic evolution. Fossils of all kinds are now of primary significance as records of the parade of evolving organisms through successive stages of earth evolution. Their great value to the stratigrapher consequently is as indicators of the relative ages of strata in an orderly succession, the identification of original sequences when the strata have become disordered by deformation, and the correlation of approximately contemporaneous formations separated by considerable distance, as between New York and Alabama in the deformed Appalachian Mountains.

The real fabric of stratigraphy began to be woven about the middle of the 18th century when some sedimentary rocks in central Europe were differentiated into thirty formations. It was a natural conclusion to the basic concept of modern stratigraphy that sedimentary rocks were deposited in orderly sequence. Within another decade it was realized that in some areas strata had been deposited upon the eroded sur-

faces of older rocks. Both marine and terrestrial fossils were soon recognized.

The most illuminating principles of stratigraphy and of geologic history were not apprehended until rather accurate geologic mapping was done by men with an interpretive outlook. In the 18th and 19th centuries, William Smith surveyed canals in the British Isles. His alert mind grasped the significance of the variable character, distribution, sequence, and fossils of the sedimentary rocks with which he worked. He fathered the concept that some beds are marked by index fossils which do not occur in associated beds. His geological map in colors, published in 1815, portrayed the areal geology of England, Wales, and part of Scotland. Geologic maps of the concentric outcrop belts of the Paris Basin had been made in the middle 18th century, but they were graphic records of observations without significant interpretation.

Structural Geology.—Observations about the structure, or attitude, of rocks were made in connection with the early mining of ores. Flat-lying strata aroused little curiosity. Highly inclined and folded strata in the mountains caused the usual fanciful theorizing.

Logical deductions based on careful observation began to supplant pure speculation in the 16th and 17th centuries, though a few scientific concepts had earlier sporadic germination. In 1688 Steno published a geological treatise in which he recognized that some strata on opposite slopes of a mountain were of the same material and had the same structural form. He conceived that some alteration in the position of strata caused mountains to be formed. Some philosophers, however, still seemed to think that mountains grew like trees.

The dogmatic Neptunists in Germany believed that inclined sedimentary rocks had been deposited originally on steep slopes and that distorted beds were due to cavern roof collapse. Hutton, the thorough observer and leader of the Plutonists in England, thought that rocks had been deformed by great lateral stresses, but he strayed from the field of rigorous observation in ascribing most deformation to igneous intrusion.

Critical observations of the highly deformed rocks of the Alps led in 1833 to the fruitful concept that the outer shell of the earth had adjusted to an interior core which was steadily shrinking because of heat loss. In consequence, great folds in the strata had been produced by lateral pressure. This far-reaching concept was supported by extensive studies, mainly by the Rogers brothers, in the folded Appalachians in Pennsylvania and Virginia. They postulated, however, that mass movements in a hypothecated internal molten mass had thrown the earth's crust into great "waves." Continued stratigraphic research by many students in the Appalachian region gave birth to the idea that enormous thicknesses of sediment had accumulated in sinking crustal troughs from which great mountain chains had been eventually upfolded and upthrust

by lateral compressive stresses. Further studies in the Alps led to a supplementary concept, that profound lateral stresses had caused great sheets of strata to be overturned, broken, and thrust forward far beyond their original positions.

Geomorphology.—Some accurate interpretations of local land forms were made by engineers and others during ancient times. They were, however, sporadic threads which did not become woven into the fabric of geology. Catastrophic convulsions of nature was the explanation of most philosophers until the development of the observational method during the Renaissance. Scientific interpretation of the characteristics, genetic relations, and evolutionary history of topographic features necessarily awaited some scientific comprehension of the stratigraphy and structure of the underlying rocks and of the creative geologic agents and processes.

The scope of geomorphologic concepts embraces most of geologic history; hence, only two basic concepts of significant illustrative value are here given brief consideration.

One of the fundamental concepts is that of the erosion cycle. In 1774 Desmarest in France propounded the doctrine that streams have cut their valleys. He also attempted to decipher the history of a landscape. Hutton in England in 1795 stated that valleys had been formed by the erosive work of sediments brought from the mountains. He broadly conceived that "there is no spot on which rivers may not have formerly run." These concepts were firmly established by Sir Charles Lyell in his excellent textbook entitled "Principles of Geology," first published in the early 1830's. He fathered the doctrine of uniformitarianism —that "the present is the key to the past;" processes of today have been the processes of all geologic time. Major Powell as a result of his trips about 1870 through the Grand Canyon country and the canyon itself believed that streams had been eroding the lands toward a featureless plain not far above sea level. About 20 years later, W. M. Davis formalized the concepts of the erosion cycle as evolutionary stages of land forms from infancy through youth and maturity to old-age characteristics. The penultimate result of stream erosion under stable crustal conditions was a peneplain. Conceptual modifications have since been made, but the essence remains.

One of the most revolutionary geologic concepts was that of continental glaciation. It is a story of long development with many facets. Its essentials were formulated in Switzerland by Agassiz just prior to the middle 19th century and applied in the United States when he became a resident here. Inasmuch as the widespread mantle of unconsolidated materials now known as glacial drift had been previously explained as due to the Noachian deluge, other great floods, and even to icebergs from polar regions, controversy was lively until well into the latter part of the century. One controversial issue was the role of alpine

glaciers versus rivers in sculpturing mountains and fiords, but in the end the proponents of the glacier sculpturing of alpine valleys proved the major aspects of their hypothesses.

Earth Age.—A most profound conceptual change in the philosophy of geology has resulted through the gradual transition from an authoritarian view of the age of the earth as a planet and as the habitat of organisms to scientific doctrine based upon critical studies of various geologic records. It is indeed a far cry from the dogma of Bishop Ussher in 1650 that the earth was created in 4004 B. C. to the modern concept that the earth is more than 3 billion years old. Lord Kelvin's calculation, based on the rate of cooling of the earth from an ancestral molten state, of 20 to 40 million years was finally found to be at decided variance with the geologic facts, but it retarded geologic concepts for a long period. Many facts entered into the new concept of the earth's age. None, however, has been as potent as the calculations based on radioactive phenomena in the slow decay of certain minerals. In brief, allantite in Nelson County, Virginia, is known to be about 800 million years old; and minerals in very ancient rocks (pre-Cambrian) in Canada to be about 2 billion years old.

As illimitable space has become available for the conceptual schemes of astronomers, almost endless time has become available to earth historians for development of concepts about the evolution of the earth and its parade of organisms.

Further Studies on the Production of Bovine Hyperkeratosis by the Administration of a Lubricant

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Evidence that bovine hyperkeratosis is caused by a toxic substance or substances is presented in the reports of various workers. Olson, Cook, and Brouse (1950) reported on an outbreak in a group of calves fed various rations. In addition to prairie hay the calves were fed various supplemental feeds that had been formed into pellets prior to the feeding trial. They obtained evidence that an unknown factor or factors in the particular dehydrated alfalfa hay and the dicalcium phosphate used in the supplement enhanced the severity of the disease. Olson and Cook (1951) later reported the production of hyperkeratosis in calves fed the pelleted feed-stuff left over from the previous work. Environment and contact were eliminated as possible factors. Olafson and McEntee (1951) were able to produce experimentally bovine hyperkeratosis by feeding a processed concentrate. Later McEntee, Hansel, and Olafson (1951) succeeded in producing the disease with the free fatty acid fraction of the ether extract of the processed concentrate. Wagener (1951) reported the production of bovine hyperkeratosis with one lot of wood preservative that was used in Germany from 1946 to 1948. Miller, Bortree, and Shook (1952) recently reported the experimental production of the disease by feeding a particular crop of timothy hay. They suggested that the hay could have been contaminated with a chemical agent possibly similar to the wood preservative used by Wagener (1951). In a previous paper the author (Bell, 1952) reported the production of hyperkeratosis by the oral administration of a lubricant. Thus, the disease has been produced under experimental conditions by use of: (1) certain alfalfa pellets, (2) a processed concentrate and fractions of this concentrate, (3) one lot of wood preservative, (4) a particular lubricant, and (5) a particular crop of timothy hay. These facts suggest that a variety of substances may become contaminated with some hyperkeratosis-producing compound. It is further indicated that the disorder may be caused by several compounds or even several groups of compounds rather than by a single entity.

Since the first report by the author (Bell, 1952) that the oral

Received for publication June 10, 1952.

administration of a lubricant could produce bovine hyperkeratosis efforts have been made to identify the active factor or factors. The work has been done in cooperation with the manufacturer, the Sinclair Refining Company and the Sinclair Research Laboratories, Inc., who furnished, in addition to financial help, the technical services of chemists, as well as the various materials used. This report describes the results obtained with the materials which represented the normal constituents of the lubricant. A chemical additive, a highly chlorinated naphthalene, used in the manufacture of the lubricant originally studied (Sinclair Opaline Chassis Lubricant), was found to produce symptoms and lesions identical with those described in the previous paper. Further cooperative studies are in progress in an effort to identify more completely the nature of this compound. It should be pointed out that as a result of this cooperative study the Sinclair Refining Company has ceased to use the highly chlorinated naphthalene as a chemical additive in the manufacture of Opaline Chassis Lubricant. Test of the lubricant as now manufactured shows that it does not produce hyperkeratosis.

MATERIALS AND METHODS

Normal calves of the Holstein, Guernsey, and Jersey breeds were obtained from the Virginia Polytechnic Institute's herds. They were fed home-grown hay, milk from the parent herd, and a commercial grain mixture for calves. The ration was identical to that used for calves in the parent herds, in which hyperkeratosis is known not to have occurred. The ages of the calves when the administration of materials was begun ranged from 61 to 140 days, and all were on the hay and grain ration at that time. The calves were all handled in the same manner except for the exposure to the various materials. No attempt at isolation was made, but in general, calves receiving the same material were penned together.

The materials furnished by the manufacturer and administered to the calves were designated as follows: (1) Item 1 — the Opaline Chassis Lubricant minus the highly chlorinated naphthalene; (2) Item 2 — A 3% solution in Mineral Oil, U.S.P., of a highly chlorinated naphthalene; and (3) Item 3 — Mineral Oil, U.S.P. These materials were administered orally by means of gelatin capsules according to the following schedule:

Calf V271 — Item 1. 10 grams each day of administration for a total of 450 grams in 57 days.

Calf 1460 — Item 2. 10 grams each day of administration for a total of 170 grams in 17 days.

Calf 1466 — Item 2. 10 grams each day of administration for a total of 160 grams in 16 days.

Calf 1476 — Item 2. 5 grams each day of administration for a total of 65 grams in 29 days.

Calf 1483 — Item 2. 5 grams each day of administration for a total of 85 grams in 22 days.

Calf 1486 — Item 2. 5 grams each day of administration for a total of 30 grams in 11 days.

Calf 1481 — Item 2. 5 grams each day of administration for a total of 15 grams in 7 days.

Calf 185 — Item 2. 5 grams each day of administration for a total of 50 grams in 12 days.

Calf 1471 — Item 3. 10 grams each day of administration for a total of 435 grams in 55 days.

Calf 1473 — Item 3. 10 grams each day of administration for a total of 230 grams in 24 days.

RESULTS AND DISCUSSION

The calf, V271, exposed by means of oral administration to Item 1 (Opaline Chassis Lubricant minus the highly chlorinated naphthalene received 450 grams in 57 days. This calf remained normal for the entire period of observation of 82 days. The amount of Item 1 administered was far in excess of that required for the production of symptoms and lesions by the lubricant previously reported (Bell, 1952). It is apparent that Item I, which is the lubricant without the chemical additive, lacked the factor or factors capable of producing symptoms or lesions under the conditions of the study.

Seven calves received varying amounts of Item 2 (a 3% solution in Minral Oil, U.S.P., of a highly chlorinated naphthalene) by means of oral administration .These calves developed symptoms and lesions identical, in most respects, to those previously reported as being produced by the lubricant. During the period of these observations no symptoms of hyperkeratosis and no evidence of a dietary deficiency appeared in approximately 30 calves remaining in the parent herd, although these calves received the same type of ration, including a grain mixture from the same source, as did the calves in the experiment.

The amounts of Item 2 administered to the calves varied from a total of 15 grams in 7 days to a total of 170 grams in 17 days. The two calves, 1460 and 1466, which received the greatest amounts of Item 2 per administration developed symptoms on the 8th and 7th days respectively, or after 80 or 70 grams had been given orally. The initial symptoms were depression and nasal discharge. These were followed by the appearance of lacrimation, salivation, and red areas on the lips, tongue, hard palate, and gums. Both calves became extremely

weak, and autopsies were conducted on the 26th day after the initial administration of Item 2. Neither calf developed pronounced hyperkeratosis, but both developed small, grayish, raised areas on the dorsal surface of the tongue and one (1466) showed similar areas of skin below the nostrils (Fig. 5).

The five other calves receiving Item 2 were given considerably less of this material than was given to calves 1460 and 1466. The first appearance of symptoms in the calves of this group varied from 12 to 17 days from the beginning of the administration of the material. Symptoms did appear, however, after as little as 15 grams of Item 2 had been given in 7 days (Calf 1481). The initial symptom in this group of five calves was lacrimation, with the exception of calf 1476, in which a reddening of the gums was the first change noted. The initial symptom was followed by intermittent diarrhea, salivation, nasal discharge, red areas at various sites such as the lips, hard palate, gums, chin, and in and around the nostrils, raised areas below the nostrils, and progressive weakness. Two calves of this group, 1483 and 1486, were autopsied on the 34th and 36th day respectively. Hyperkeratosis or proliferative changes, except raised areas on the chin of Calf 1483, were not pronounced in these two animals. Calf 1476 developed pronounced proliferative changes on the dental pad (Figs. 1, 2, 3) and at the border of the right nostril (Fig. 4) and a definite thickening of the skin before autopsy on the 40th day. Calf 185, which received a total of 50 grams of Item 2 in 12 days, developed a pronounced thickening of the skin (Figs. 9, 10) and erosions and proliferations of the tongue by the time of autopsy on the 52nd day.

One calf of this group of five that received the small amounts of Item 2 was still alive on the 52nd day. This calf, 1481, which received a total of 15 grams in 7 days, had a continuous profuse lacrimation that began on the 12th day and a progressive thickening of the skin of the neck. The dental pad and upper lips became rough, and the gums acquired a rough, wart-like appearance. It should be pointed out that each calf did not necessarily show all the symptoms described, but that the symptoms reported represent the changes observed in the calves as a group.

The six calves receiving Item 2 that have been sacrificed presented the same picture at autopsy. In addition to the changes already noted, gross changes were found in the digestive tract, liver, gall bladder, and urinary tract. Flat ulcers were present in the abomasum of three calves, and two calves had several areas of hemorrhages in the walls of the small intestines. The livers of four calves had light-colored areas on the surface, extending into the parenchyma, and in calf 185 there was marked proliferation and dilatation of the bile ducts and fibrosis of one lobe. The gall bladder was distended in all cases,

with apparently thickened walls. On the mucosa of four gall bladders were found numerous nodules, and the bile ducts of calf 185 showed nodular proliferations of the lining. In one calf there were extensive hemorrhages beneath the mucosa of the common bile duct. The kidneys in all calves were slightly enlarged and pale in color, and on section the cortex was found to be markedly striated.

Examination of tissues obtained at autopsy revealed histological changes in agreement with those previously reported (Bell, 1952). Cystic dilatation of the tubules in the kidney cortex (Fig. 6) was the most pronounced change and was observed in all cases. Varying degrees of bile duct proliferation (Fig. 7) were also observed in most liver sections. Cystic dilatation of the glands of the gall bladder (Fig. 8) occurred in some instances, and a proliferative lesion in the gall bladder was present in one calf. An accumulation of keratinized material and keratinization of hair follicles was not pronounced except for calves 1476 and 185. The kidney changes were uniform, but the other changes were not necessarily observed in each of the six calves examined.

The course of the condition produced by Item 2 was rapid and similar to that produced with the original lubricant. The duration, under the conditions of study, ranged from 26 to 52 days for six of the seven calves receiving Item 2. One other calf, which received 15 grams, is still living at 53 days. This calf, 1481, received the smallest amount of Item 2, which may account for its survival for the longer period. This suggests the use of larger animals or smaller amounts of the material might result in a more prolonged and chronic syndrome. No attempt was made to determine the minimum amount necessary to produce symptoms, and it is apparent that in most cases an amount considerably in excess of that needed to produce symptoms was administered. Some indication of minimum amounts may be gained from Calf 1481 which received 15 grams of Item 2 during a period of 7 days and presented symptoms on the 12th day. This quantity contained 0.45 grams of the highly chlorinated naphthalene.

In no instance did the cessation of administration of Item 2 result in improvement of the condition of the calves. The time of appearance of the first symptoms, subsequent developments, and the duration of the disease produced are identical, in most respects, with the data previously presented (Bell, 1952) and are in general agreement with the results obtained by McEntee, Hansel, and Olafson (1951) with the fraction of a processed concentrate.

The two calves that received Item 3 (Mineral Oil, U. S. P.) remained normal during the period of observation. Calf 1471 received 435 grams in 55 days and was observed for a total of 82 days. The amount of Item 3 given was considerably in excess of the amount of Item 2 necessary for the production of symptoms and lesions. Calf 1473 was accidentally killed on the 24th day after having received 230 grams

of Item 3. No symptoms had been observed, and no lesions similar to those observed in the calves given Item 2 were found. It appears that the Mineral Oil, U. S. P., used as the vehicle for the highly chlorinated naphthalene, was harmless and that the effects produced by Item 2 were not related to the vehicle.

Although it has been shown that a highly chlorinated naphthalene, which was used as an additive to a lubricant, produced the same symptoms and lesions as the lubricant containing the compound, it cannot be assumed that all such compounds are toxic. At the present time it must also be recognized that several compounds or even different groups of compounds may possibly be capable of producing bovine hyperkeratosis. All petroleum products or lubricants do not necessarily contain the compounds used in this study, and it should not be assumed that the other materials found capable of producing hyperkeratosis contain it. Until identity of the active factor or factors is established it is wise to avoid unnecessary exposure of animals to products of a petroleum nature.

SUMMARY

Symptoms and lesions have been produced in calves, by the administration of a highly chlorinated naphthalene, that were identical to those produced by a lubricant containing this material. Although a prolonged chronic disease was not produced in most instances, the symptoms and lesions are in general agreement with those reported by others as being characteristic of bovine hyperkeratosis. Calves receiving a lubricant that did not contain the material or receiving Mineral Oil, U. S. P., which was used as a vehicle, remained normal. Approximately 30 calves in the parent herd during the period of observations, which were fed the same ration as the experimental calves, showed no hyperkeratosis or dietary deficiency.

ACKNOWLEDGMENTS

The author wishes to express his appreciation to the Sinclair Refining Company and the Sinclair Research Laboratories, Inc. for financial aid, technical assistance and advice; to Dr. H. S. Mosby, V. P. I., for photographs; to Miss B. V. Conner, V. P. I., for the photomicrographs; to the V. P. I. Animal Husbandry, Dairy Husbandry, and Agronomy Department for making feed and calves available; and to Dr. A. M. Lee, U. S. D. A., B. A. I., for his advice and counsel.

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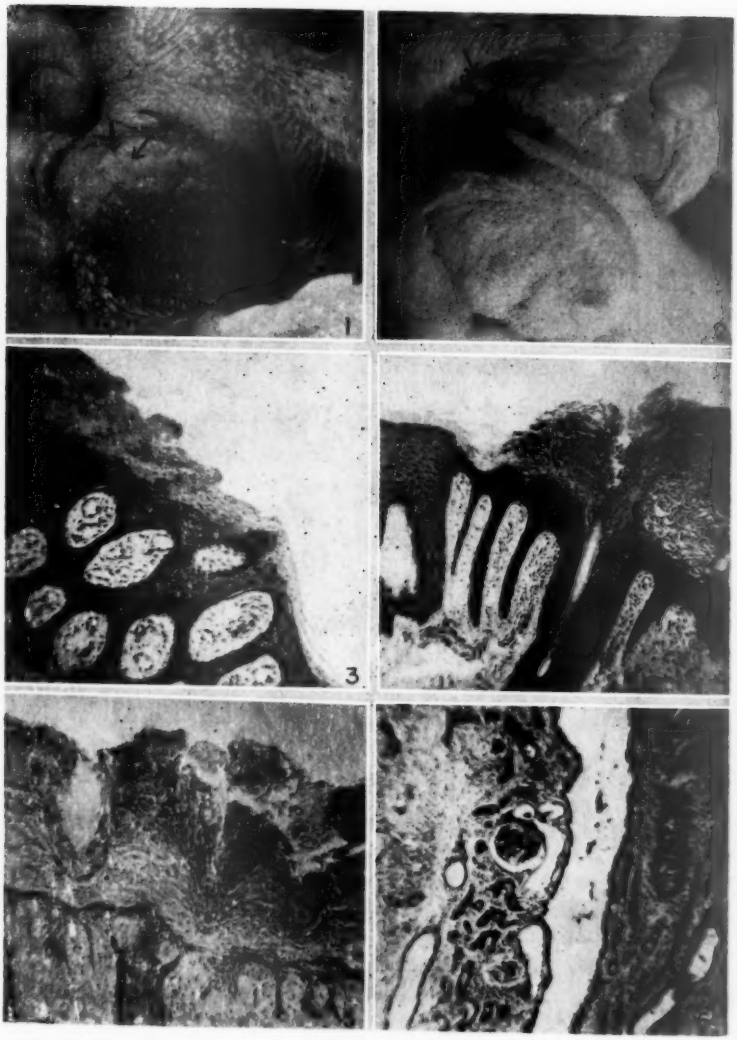
LEGEND FOR FIGURES

Fig. 1—Calf 476. Proliferation of dental pad on 34th day. Fig. 2—Calf 476. Proliferation of dental pad and oral mucosa on 40th day. Fig. 3—Calf 476. Section of proliferative lesion of dental pad. Fig. 4—Calf 476. Section of proliferative lesion in right nostril. Fig. 5—Calf 466. Section of proliferative lesion in skin below right nostril. Fig. 6—Calf 476. Section of kidney showing dilatation of tubules. Fig. 7—Calf 476. Section of liver showing bile duct proliferation. Fig. 8—Calf 460 Section of gall bladder showing dilatation of glands. Fig. 9—Calf 185. General appearance on 37th day. Fig. 10—Calf 185. Hyperkeratosis and lacrimation at 50th day.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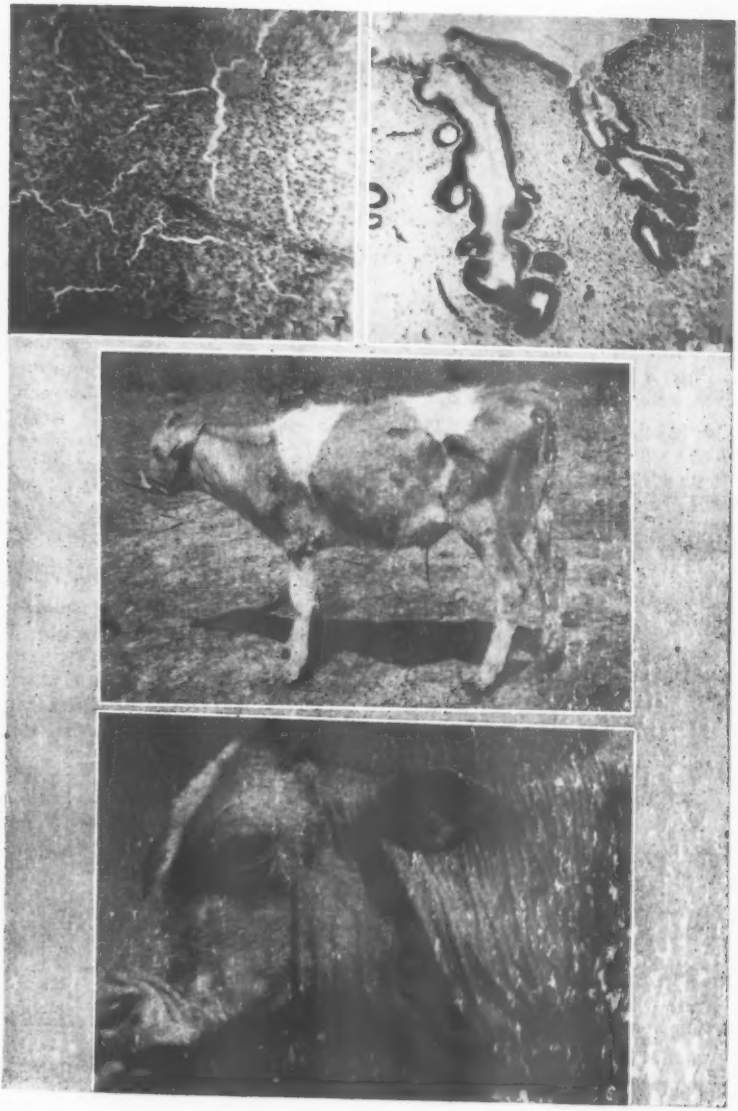


can be used with a satisfactory amplifier and potentiometer even at quite low moisture levels of soils.

In the work here described use was made of the Donnan membrane equilibrium to determine the cation activities and diffusible electrolytes of clay suspensions. H-clays were saturated to different degrees with single cations and with mixtures. Activities of Ca, K, Na, and H were then determined.

THEORETICAL CONSIDERATIONS

The determination of ion activities in a colloidal suspension by means of the Donnan membrane equilibrium depends on the principle that for a system of ions undergoing thermal motion each ionic species at equilibrium will have the same electrochemical potential throughout the system. Thus, the system may consist of a clay suspension (the presence of some free electrolytes being permitted) designated as phase (') separated from a water solution, phase ("), by a membrane which is impermeable to the colloidal particles but which allows the free diffusion of all other ions. If there is no significant movement of water from one phase to another and sufficient time is allowed, the system will fulfill the requirements of a Donnan equilibrium. Although the clay suspension is not an ideal solution it must be emphasized that the suspension of charged clay particles is the same in principle as an ionic solution.

Owing to the facts that the colloidal particles are not diffusible, while associated cations are, an electrical double layer exists in the region of the boundary between the phases. An electrical field thus exists perpendicularly to the phase boundary. Electrical work is required to carry a unit charge across this double layer, and a potential difference thus exists between the phases. We will refer to this potential as the membrane potential.

Starting with the thermodynamic relationship

$$dF = - SdT + \bar{V}dP + \Sigma_i \bar{\mu}_i dn_i$$

where F is the free energy of Lewis; S the entropy; T the absolute temperature; $\bar{V}$ the partial mold volume of the chemical species i; P the pressure; $\bar{\mu}_i$ the electrochemical potential; and n_i the number of moles of chemical species i, we may derive the Donnan equation.

At constant temperature and pressure the conditions for equilibrium are given by

$$dF = 0 = \Sigma_i \bar{\mu}_i dn_i$$

The above equation states that the electrochemical potential of ionic species i in phase (') must equal that of i in phase (") at equilibrium.

The electrochemical potential consists of a chemical component u_i and an electrical component $Z_iF\psi$ where Z_i is the valence of species i, F is the Faraday, and ψ is the electrical potential of the phase containing species i. Or

$$\bar{\mu}_i = \mu_i + Z_iF\Psi \text{ or}$$

Therefore since $(\bar{\mu}_i)' = (\bar{\mu}_i)''$ at equilibrium, then

$$(\mu_i)' + Z_iF(\Psi)' = (\mu_i)'' + Z_iF(\Psi)'' \quad \text{or}$$

$$Z_iF(\Psi''-\Psi') = (\mu_i)' - (\mu_i)''$$

But $\mu_i=\mu^\circ_i+RT\ln a_i$ where μ_i is the chemical potential of i; μ°_i a constant depending on temperature and pressure; a_i is the osmotic activity of species i.

Finally:

$$\Psi'' - \Psi' = \frac{RT}{Z_iF} \ln \frac{a_i'}{a_i''} \qquad \psi'' - \psi' \text{ is the membrane}$$

potential and will be designated as E_m.

It will be noted that the chemical potential μ_i is not equal at equilibrium between the phases.

Since the anions Z_i is negative the reciprocal of the activity ratio holds for all anions of the system except the clay particles.

Therefore for all diffusible ions the Donnan ratios hold as follows:

$$\frac{a'_{M_1}}{a''_{M_1}} = \frac{a'_{M_2}}{a''_{M_2}} = \frac{a'_{M_3}}{a''_{M_3}} = \frac{a''_{A_1}}{a'_{A_1}} = \frac{a''_{A_2}}{a'_{A_2}} \text{ etc.}$$

where M represents cations and A anions.

In the absence of the membrane the same basic principle of equal electrochemical potential for a given ionic species throughout the system at equilibrium holds. Gravity or other restraining forces may act on the relatively large colloidal particles to prevent their homogeneous distribution. The electric forces in the colloidal surfaces will be the only restriction on the free diffusion of the associated cations.

The relationship between the colloidal particles and the associated ions can be seen from the kinetic point of view as follows: The suspended particles may be regarded as great ions with relatively high charges made electrically neutral by a swarm of normal sized ions of opposite charge. These ions possess kinetic energy and therefore a mathemati-

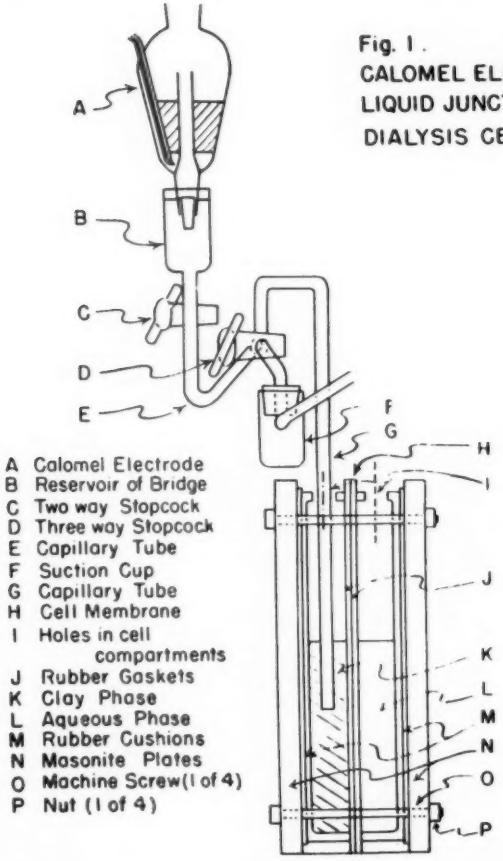


Fig. 1.
CALOMEL ELECTRODE
LIQUID JUNCTION BRIDGE
DIALYSIS CELL

angles by smaller copper tubes. Rubber tubes connected these to glass compartments into the suspensions and solutions. The air was scrubbed through a 10% H_2SO_4 trap and three traps of distilled water. Rate of air flow was controlled with screw clamps on the rubber tubes.

To measure the membrane potential, E_m, the difference between the electromotive potentials of two saturated potassium chloride calomel electrodes was determined. Salt bridges of saturated potassium chloride were used. In order to minimize liquid junction potentials between the salt bridges and the phases cylindrical junctions of the free-diffusion

type were formed by means of a three-way stopcock in a specially constructed bridge. One bridge is shown in Fig. 1. The capillary tube, G, was inserted into the phase to which the electrode was to be connected. The phase (clay suspension or aqueous solution) was then drawn into the 2 mm. capillary tube, G, connected through the three-way stopcock, D, with the suction cup, F. The stopcock plug was then turned to connect the reservoir, B, to the suction cup, F, and the bore of the stopcock plug was thoroughly flushed of the phase with saturated KCl. A second stopcock, C, (only two-way) was closed when the reservoir, the 2 mm. capillary tubing connecting the reservoir with the three-way stopcock, and the bore of the three-way stopcock plug were completely filled with saturated KCl, and no air bubbles were present. The two-way stopcock plug was rotated enough so that sufficient saturated KCl was between the plug and the receptacle to conduct a current even though no KCl could flow. The three-way stopcock plug was then turned until the saturated KCl was connected to the phase, thus making a sharp junction. In the same way a saturated potassium chloride calomel electrode was connected to the other phase.

The two electrodes were then connected to the terminals of a Leeds and Northrup thermionic amplifier which was used in conjunction with a student potentiometer and a Leeds and Northrup 2420 C Galvanometer. The electrodes and other parts of the circuit external to the amplifier-potentiometer-galvanometer system were shielded. This is essential when the resistance of the system being measured exceeds 10 megohms. The equipment described permits measurements of potentials with an accuracy of 0.2 millivolt.

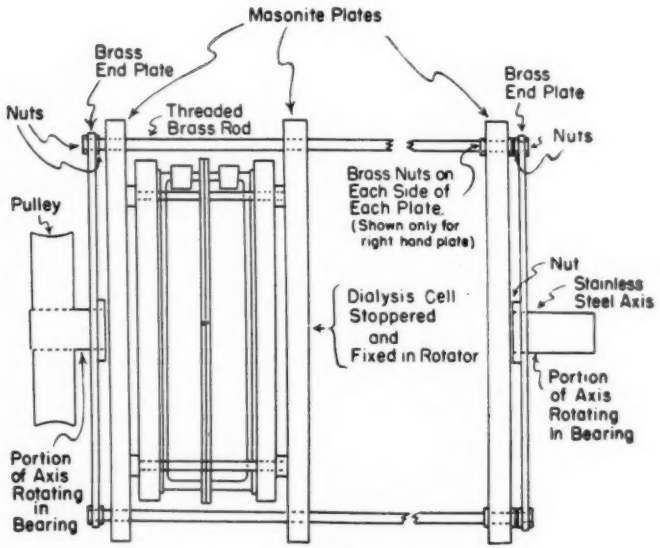
Analysis of the Aqueous Phase.—The aqueous phase was analyzed with the flame photometer. For the determination of calcium by this method it was necessary in some cases to concentrate the solution prior to atomizing it in the flame. To a known volume of the aqueous phase 3 cc. of concentrated HNO_3 were added and the solution was evaporated to dryness. The residue was taken up in 0.05 N HNO_3, made to a desired volume, and allowed to stand to permit dehydrated silica to settle out.

With the Perkins-Elmer flame photometer sufficient lithium salt was added to make the final solution 40ppm. of lithium, the internal standard.

To solutions analyzed for Na sufficient Ca and K salts were added to make the final solution 0.004 M with respect to these cations; to solutions analyzed for K enough Na and Ca salts were added to make the final solution 0.004 M with respect to these cations; Ca solutions for analysis were made 0.004 M with respect to Al, K, and Na.

Standards with which the unknowns were compared were made up to contain the same concentration of compensating ions as the unknowns.

Fig. 2
ROTATOR WITH ONE DIALYSIS CELL
(Front view)



Prepartion of Clays.—A 3% suspension of montmorillonite <lu and a 5% suspension of Mardin clay <0.2u (Mardin soil series) were the clays investigated. These colloidal fractions were separated by sedimentation or by sedimentation and centrifuging through a Sharples centrifuge. After preparation of the H-clays by electrodialysis, potassium, sodium, and calcium clays of varying degrees of saturation were prepared with the respective hydroxides. In addition clay suspensions containing mixtures of cations and mixtures of the chlorides of sodium, potassium, and calcium were studied.

Procedure.—The dialysis cells were assembled and carefully tightened until watertight. They were then allowed to stand filled with distilled water for two days. The water was changed approxi-

mately eight times during the two days to remove any electrolytes in the membranes. The cells were then drained. The clay suspension was introduced into one compartment through the 7 mm hole in the rim and simultaneously the distilled water or salt solution was introduced into the other compartment. Equal volumes of the two phases were used. The phase volumes varied from 100 cc. to 190 cc.

When all the cells were filled the hole in each compartment was stoppered and the cells fixed between the rotator plates. Rotation was carried on for the desired length of time. If the equilibrating systems called for aeration, the rotator was stopped, the stoppers removed, and air at a controlled rate was passed through for an hour and a half. The cells were rotated for 12 hours after aeration before the membrane potentials were measured. A total period of equilibration of five days was allowed prior to determining the membrane potentials.

As soon as these measurements were made, the contents of each compartment were removed with pipettes and the respective volumes determined. The aqueous phase was stored in stoppered 125 cc. Pyrex glass Erlenmeyer flasks prior to analysis.

EXPERIMENTAL RESULTS

Relations Between a'_M, a''_M, E_m, and Diffusible Electrolytes.— In Table I and Fig. 3 are shown the changes of the membrane potential with time for K and H- montmorillonite. The potential at the start will be called the diffusion potential, and the potential at equilibrium the membrane potential, E_m. The data show that the potential drops very rapidly at first, but after 96 hours the drop in potential is in no case greater than 1.3 millivolts per 24 hours. Obviously, from Fig. 3, a very long time is required to reach the point at which no further change in the membrane potential and a''_M occurs. This point was probably not reached after two weeks.

It is seen that for H-montmorillonite pH' is constant while pH'' and E_m both decrease with time. For K-montmorillonite a'_K remains constant and a''_K increases while E_m decreases. Since pH' remains constant after 48 hours and a'_K after 72 hours, the time of equilibration after which the membrane potential is measured and the aqueous phase is analyzed is not critical. a'_M can be correctly determined at widely different times and show little change.

Fig. 3. EQUILIBRATION CURVES

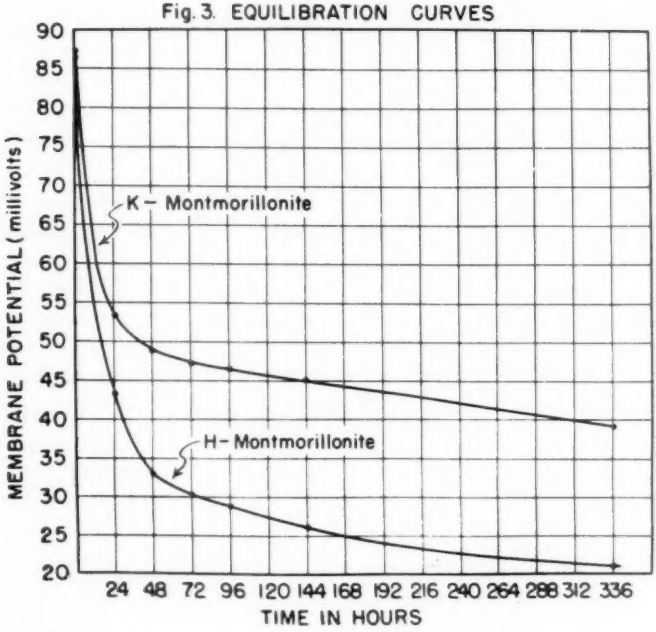


TABLE I. Change in Membrance Potentials and Ionic Activities with Time.

Time	Membrane Potentials (millivolts)		pH'	pH''		
	Cell No. 1	Cell No. 2	Cell No. 1			
1 hr.	86.6	85.6				
24 hrs.	42.8	43.6				
48 hrs.	32.7	34.2	3.25	3.80		
72 hrs.	30.1	30.1				
96 hrs.	28.6	27.3	3.25	3.70		
144 hrs.	28.7	26.0	3.30	3.70		
336 hrs.	21.2	21.0	3.25	3.60		
	Cell No. 3	Cell No. 4			A''_K	A''_K Cell No. 3
1 hr.	87.1	87.0				
24 hrs.	53.4	52.3				
48 hrs.	48.8	48.5				
72 hrs.	47.2	47.1			0.0052	0.00085
96 hrs.	46.5	44.7			0.0053	0.00091
144 hrs.	45.2	44.0			0.0052	0.00094
336 hrs.	39.1	37.7				

The gradual but steady increase of a''_M in all instances for the montmorillonite clays and for Mardin clays other than those containing Ca is significant in these results. The extent of this change is a measure of the diffusible electrolytes in the respective clays. Although part of the diffusible electrolytes are due to hydrolysis of the bases on the clays, data for the H-montmorillonite and for the Mardin clays in general indicate that components of the clay are soluble. In certain instances this solution continues until a''_M exceeds a'_M (E_m becomes negative). This is seen to be true for H-Mardin clay (Table II) where the diffusion potential or the potential at the beginning of the equilibration changes from positive to a negative E_m (i.e., the aqueous phase is negative) at equilibrium. For Mardin clays 50% Ca+50% H and 100% Ca and 150% Ca the diffusion potentials are negative. E_m is also negative but of smaller magnitude than the diffusion potentials for each of the latter two clays. Montmorillonite clays shows a negative membrane potential only for the 150% Ca system.

TABLE II. Diffusion Potentials and Membrane Potentials of Clays with Different Cations and Degrees of Saturation

Clay	% Concentration	Cation Exchange Capacity M.E./100gm.	Cation on Clay and % Saturation	Diffusion Potential millivolts both measured in the absence of membrane: initial	Membrane Potential millivolts both measured in the absence of membrane: final	Membrane Potential final millivolts measured in the presence of membrane
Montmorillonite or Wyoming Bentonite <0.1u fraction	3.0	75	100% H	86.6	28.7	28.7
	3.0	75	100% K	87.1	45.2	44.8
	3.0	75	150% Ca			-2.4
Mardin Clay <0.2u fraction	5.0	70	100% H	22.0		-4.8
	5.0	70	100% Ca	-46.0		-7.9
	5.0	70	50% Ca	-29.8		-11.8
	5.0	70	100% K	27.5		5.2
	5.0	70	50% K	18.2		10.2

Na+50% H system. For the (40% Na+10% K+50% Ca) clay, K activity is less than one-tenth that of the 50% K+50% H clay. Thus under comparable conditions in clay suspensions with Na, Ca, and K all present Na activity is much greater than K activity. This is true for all degrees of saturation used for the mixed cation clays.

At 50% saturation, the calcium activity in the Mardin clay remains relatively constant with variation in K and Na, but this calcium activity is approximately six times as great as calcium activity in the 50% Ca+50% H clay.

In summary the activities of Na and K are greater for the Mardin clay than for the montmorillonite. Activity of Ca is greater for montmorillonite except for the 100% Ca degree of saturation. For the 100% Ca saturated clays Ca activity is greater for the Mardin clay. H activity is much greater for H montmorillonite than for H Mardin colloid.

It should be pointed out that the montmorillonite suspension contained 3.0% clay whereas the Mardin clay suspensions contained 5.0% or 6.7% clay.

The Mardin potassium-saturated clay suspension at 6.7% concentration showed a slight increase in activity of K over the suspension containing 5% clay.

Fraction of Cation Active.—Fractions of the cation active or the cation activity coefficient in the clay phase are given in Table IV.

In general it is seen that for each clay suspension in which only one base is present the fraction of the cation active is of similar magnitude for Na and K ions for each degree of saturation. These fractions active increase with increasing degree of base saturation of the clay.

The fraction of H active in H-montmorillonite is somewhat greater than that of Ca in the Ca-montmorillonite. For the Mardin clay the fraction active of Ca in the Ca-clay is ten times as great as the fraction of H active in H-clay. In the case of montmorillonite the fraction of Ca active decreases as the calcium saturation of the clay increases from 50% to 100%. The 150% Ca saturated clay shows a marked increase of about three-fold in fraction of Ca active (over the 100% degree of Ca saturation). In the case of the Mardin clay the fraction of Ca active increases with increasing degree of saturation although the highest fraction active is only 0.03.

When the montmorillonite clay, 50% Ca+50% K saturated, is compared with the clay 50% Ca+50% H it is seen that the calcium fraction active is slightly increased by substitution of K for H. It is also seen that the substitution of Ca for H in 50% K clay has increased the fraction of K active by almost fifty per cent.

Mardin clay, with the degree of calcium saturation held at 50% and with K and Na together making up the other 50% in varying ratios of Na to K, shows a remarkable two-fold increase in fraction of Na

TABLE IV. Fraction of Cation Active in Suspensions of Clay at Different Degrees of Saturation with Three Different Cations and with Mixtures of Cations.

Clay	%Concentration	Cation Exchange Capacity ME/100 gms	Cation on Clay	$\frac{a'_M}{(c'_M)_f}$* = Fraction active at the following degrees of saturation						
				50%	100%	150%	50%Ca 50%K	50%Ca 10%Na 40%K	50%Ca 25%Na 25%K	50%Ca 40%Na 10%K
Montmorillonite (Wyoming Bentonite) <1u fraction	3.0	75	Na	0.200	0.281	0.354				
	3.0	75	K	0.254	0.273	0.408				
	3.0	75	Ca	0.040	0.026	0.071				
	3.0	80	K				0.364			
			Ca				0.050			
	3.0	75	H		0.032					
Mardin Clay <0.2u fraction	5.0	70	Na	0.232	0.349	0.420				
	5.0	70	K	0.218	0.360	0.395				
	5.0	70	Ca	0.019	0.025	0.029				
	5.0	70	Na					0.501	0.532	0.441
			K					0.199	0.143	0.087
	5.0		Ca					0.160	0.139	0.153
	5.0	70	H		0.003					
	6.7	70	K		0.304					

* subscripts f denotes final concentration.

is more than twice as great as that of 100% saturated Ca clay.

Na-Mardin clay shows a decreased degree of dissociation at degrees of sodium saturation greater than 50%. The fraction of total Na activity of the clay suspension that is due to diffusible electrolytes increases to 0.88 at 150% sodium saturation. The degree of dissociation of K-Mardin clay increases slightly when the percentage of K saturation is increased from 50% to 100%. The degree of dissociation of K-Mardin clay is the same at 100% and 150% K saturation. Increasing the concentration of the Mardin potassium saturated clay from 5.0 to 6.7% slightly decreased the degree of dissociation of the potassium cations.

As can be seen in Table IV the fraction of Na and K active for the Mardin clay are in general greater than the same fractions active for montmorillonite. The degrees of dissociation (Table VI) of Na and K of the Mardin clay, however, are much smaller in everyinstance than are the same degrees of dissociation for montmorillonite.

Since H-Mardin clay suspension equilibrated with water has a negative membrane potential, the net dissociation of H-Mardin clay is indicated to be very small. H-montmorillonite is 0.03 dissociated.

Montmorillonite shows a greater degree of dissociation of cations in all instances investigated than does Mardin clay.

Clay	%Concentration	Cation Exchange Capacity ME/100gms	Cation on Clay	Degree of Dissociation of Cations at the following degrees of saturation. 50%	100%	150%
Montmorillonite or Wyoming Bentonite	3.0	75	Na	0.176	0.264	0.302
	3.0	75	K	0.247	0.266	0.354
	3.0	75	Ca	0.025	0.015	§
	3.0	75	H		0.029	
Mardin Clay	5.0	70	Na	0.108	0.066	0.078
	5.0	70	K	0.133	0.158	0.154
	5.0	70	Ca	§	§	§
			H		§	
	6.7	70	K		0.135	

* Degree of dissociation $= \frac{Z}{(\text{M clay})_f}$

for H, Na, and K: $Z = a'_M - Y$; $(\text{M clay})_f = (C'_M)_f - Y$

for Ca $Z = a'_M - \frac{Y}{2}$; $(\text{M clay})_f = (C'_M)_f - \frac{Y}{2}$

Note: subscript f denotes final concentration

§ According to the explanation suggested in this work these net values should approach zero.

In the equilibration of clay suspensions containing more than one cation the diffusible anions in the clay cannot be apportioned to the different cations. Therefore, here the relative degree of dissociation must be inferred entirely from the fraction of cation active.

TABLE VI. Degree of Dissociation * of Cations From Two Clays at Different Degrees of Saturation.

DISCUSSION OF RESULTS

Schofield (1949) has advanced the opinion that the buffering observed when an acid clay suspension is titrated with alkali is due to the aluminum ions liberated during the preparation of the acid clay and then held as exchangeable ions. These exchangeable aluminum ions react with the hydroxyl ions of the alkali used in the titration principally in the range of pH between 4 and 5 and are precipitated as aluminum hydroxide. Schofield demonstrated that a component of an acid clay suspension consisting mainly of hydrous ferric oxide carried positive charges at a pH of 3 but not at pH 7.

In the work described here a net positive charge in the Mardin clay suspension was observed at a pH of 6.2 and 7.4. Assuming that exchangeable aluminum was precipitated at pH 6.2 and also 7.4 and was still dissociated (as aluminum hydroxide) to a greater extent than either the exchangeable aluminum or exchangeable calcium on the clay, then a net negative diffusion potential should have been found. Where the clay was only 50% Ca saturated a greater proportion of Al and Ca ions in exchangeable form should reduce the net negative diffusion potential (increase it positively). These relations were observed.

Where the clay was either acid (electrodialyzed) or 50% and 100% saturated with K, positive diffusion potentials were observed. For the acid clay the dissociation of echangeable aluminum should produce a positive diffusion potential. Likewise the greater degree of dissociation of the K+Al (clay) and of the K clay (as compared with the dissociation of aluminum hydroxide) should cause a net positive diffusion potential. That K is relatively more dissociated from clays than Ca is indicated by the known greater ease of displacement from exchange positions.

The reversal of sign of the acid clay from a positive diffusion potential (Mattson *et al.*, 1940) to a negative equilibrium or membrane potential indicates the passage of soluble aluminum in perhaps the form of the hydroxide, the silicate, and the humate (Mardin soil clay) into the aqueous phase. If the hydrolysis of Al and its diffusion into the aqueous phase resulted in a greater degree of dissociation of Al in the aqueous phase than the net dissociation of replaceable Al in the clay phase then a negative membrane potential should be found. These interpretations are in accord with the data.

It is clear that montmorillonite differs in these specific relations.

According to Schofield this clay behaves more nearly as a weak acid than do the ordinary clays of soils. This is borne out in the results of this paper.

The Donnan technique appears to afford a means for studying the so-called isoelectric points of soils (Mattson *et al*, 1940).

Degree of dissociation and hydrolysis of cations from clays are commonly considered to affect directly the absorption by plants of the cations in question. Previous information concerning the relative dissociation of cations on different clay minerals is largely based on the work of Marshall and co-workers (Marshall, 1942). As has been pointed out they used clay membrane electrodes to determine total cation activity in clay suspensions. Their method does not permit the resolution of the total cation activity observed in a clay suspension into the fraction due to dissociation and the fraction due to diffusion of electrolytes. Furthermore, since the electrodes used by them were nonspecific in a clay suspension having several co-existing cations, the cation activity could be determined only for clay suspensions with one or two cations present.

Insofar as the work described here parallels that of Marshall *et al.* (1950), results given here confirm their findings. For example, it was found that the fraction of cation active was much greater for both Na and K than for Ca for both clays studied. Likewise it was found that the fraction of H active was very much greater for H-montmorillonite than for H-Mardin clay. The greater degree of dissociation of H-montmorillonite is in accord with Marshall's findings, in view of the following order established by him for the decreasing degree of ionization by hydrogen from clays: montmorillonite> beidellite> illite> kaolinite (Marshall, 1942). It may be observed in Table IV that for Na and K in general the fraction active decreases from Mardin clay to montmorillonite. Mardin clay is believed to consist of a mixture of kaolinite and illite. The order established by Marshall for the dissociation of Na- and K-clays is kaolinite> montmorillonite> beidellite> illite. Marshall found that on the average the extent of ionization of potassium from kaolinite was not greatly different from that from montmorillonite. This is likewise noted in the results given here when degree of ionization is inferred from fractions active of K in the clay suspensions.

With this technique based on Donnan equilibrium used in this study it has been possible to get information not previously available. The apportionment of the observed total cation activity in the clay suspension to dissociation and the presence of soluble electrolytes presents a different picture of the relative degree of dissociation of cations from the two clays.

Hitherto, a large fraction of cation active has been interpreted to indicate a large degree of M-clay dissociation. It now appears that

this may well be due to soluble components of the electrodialyzed clay suspension. In the light of the work by Mehlich and Colwell (1943) on the absorption of Ca by plants from media containing kaolinite and montmorillonite, the greater uptake of Ca from the kaolinite media would be due to the greater content of diffusible electrolytes.

A logical consequence of the net positive charge on the clay is the adsorption of phosphates in the pH range of 6.2 to greater than 7.0. This would explain the known phosphate adsorption in this middle pH range. In the case of the Mardin colloid, phosphate ions would be adsorbed at a lower pH (or lower degree of Ca saturation) than for montmorillonite, since the net cation dissociation from Ca-Mardin clay even at 50% saturation (pH 6.25) is suppressed to such an extent that the membrane potential is negative. A negative membrance potential for montmorillonite and thus a net positively charged clay suspension was observed only at 150% Ca saturation.

Results of Schofield (1949) indicate that the anion exchange capacity of soil clays increases with acidity. That the nature of the anion effects its tightness of retention by clays is well known. Barbier and Chabannes (1948) have shown that maximum absorption of anions occurs after flocculation. This indicates that the double layers of the positively and negatively charged colloidal particles must be compressed so that there is no interpenetration of the layers before maximum anion absorption occurs. Thus anion adsorption is greater at high concentration of electrolytes.

In the case of both montmorillonite and Mardin clay, the fraction of the total observed cation activity due to the presence of diffusible electrolytes was less for the potassium systems than for the comparable calcium systems. Therefore, it should follow that supplying a soil with at least 50% Ca should increase the K in solution, and the presence of K should decrease the soluble Ca in a soil.

Many investigations of the plant root environment have dealt with either soil extracts taken with different moisture percentages or with "soil solutions" separated from the soil by displacement or by a pressure membrane method. It had been thought that such studies neglected the role of the solid phase of the soil. Thus it was believed that these studies provided a much less complete picture of the ionic environment of plants in humid region soils than they did of this environment of plants in arid region soils. It appears from the result of the work described here that the soil solution is of major importance in the nutrition of plants in the humid region soils.

SUMMARY

The dissociation and diffusion of soluble electrolytes from montmorillonite and Mardin clay were studied by means of the Donnan membrane equilibrium. Diffusion and membrane potentials of clay sus-

pensions were determined. An interpretation of these diffusion and membrane potentials in the light of probable components of the clay suspensions has been suggested. Activities of cations of hydrogen clays as well as of clays that had been 50%, 100%, and 150% saturated with Na, K, or Ca were determined. The activities of cations were also determined in clay suspensions containing K and Ca, or Na, K, and Ca.

Fractions of cations active were calculated. Activities due to diffusible electrolytes and degree of dissociation of M clays were estimated using the Donnan activity product principle.

Practical consequences of the results are suggested.

ACKNOWLEDGMENTS

The writer wishes to express great appreciation to Dr. Michael Peech of Cornell University for introducing him to the problem and for his guidance in the research. The conclusions and opinions expressed herein are the author's own.

Appreciation is expressed also to Mr. Ralph Olsen, for the analyses with the flame photometer.

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Size Variations and Sexual Dimorphisms in a Brood of Common Garter Snakes, *Thamnophis o. ordinatus* (L.)[1]

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No systematic study of the scutellation and sexual dimorphisms of a brood of Common Garter Snakes, *Thamnophis o. ordinatus* (L.) has been published, though Fisher (1928) investigated these matters in the Pacific states' subspecies, *Thamnophis ordinatus infernalis* (Blainville). Pope (1944) reported an even more suprising fact in pointing out that few broods had even been accurately measured.

Total lengths of new-born specimens have been reported by Conant (1938), Pope (1944), Wood (1945), and Mattlin (1948), but the question of whether there is any difference between the sexes in size at time of birth has not been previously investigated. Reported here are the measurements and scale-counts of 48 from a brood of 59 *Thamnophis o. ordinatus* born July 30, 1950 of a female collected three miles north of Hilton Village, Warwick County, Virginia by Philip Hancock. The 11 specimens not included in this study died shortly after birth, failing to emerge from their embryonic membrances.

The 48 specimens studied consisted of 26 males and 22 females. Total lengths of males ranged from 142.5 to 165.5 mm., averaging 153.6 $\pm$5.8 mm.[2]; those of females, from 134.0 to 157.0, averaging 147.0$\pm$4.7 mm. At time of birth the average length of males in this brood exceeded the average length of the females present. The head and body lengths of these specimens showed far less difference at time of birth. Head and body lengths of males ranged from 109.0 to 124.0 mm, averaging 116.9$\pm$4.3 mm.; those of females ranged from 104.0 to 121.5 mm., averaging 115.1$\pm$3.8 mm. The total lengths and head and body lengths (snout-vent lengths) of these specimens are plotted in figure 1. Note that males and females occupy nearly discrete groupings, indicating that a sexual dimorphism other than a difference in average total lengths is present, a difference in

1. Formerly designated **Thamnophis s. sirtalis** (L.), the Common Garter Snake has been verified as **ordinatus** by Klauber (1948). By the rules of priority the name **sirtalis** belongs to the Ribbon Snakes, formerly known as **Thamnophis s. sauritus** (L.).

2. Work on this report was completed when the senior author was a staff member of the Virginia Fisheries Laboratory and the Department of Biology of the College of William and Mary.

3. Standard deviations follow the averages (means) in all cases where the "plus or minus" signs are used in this report.

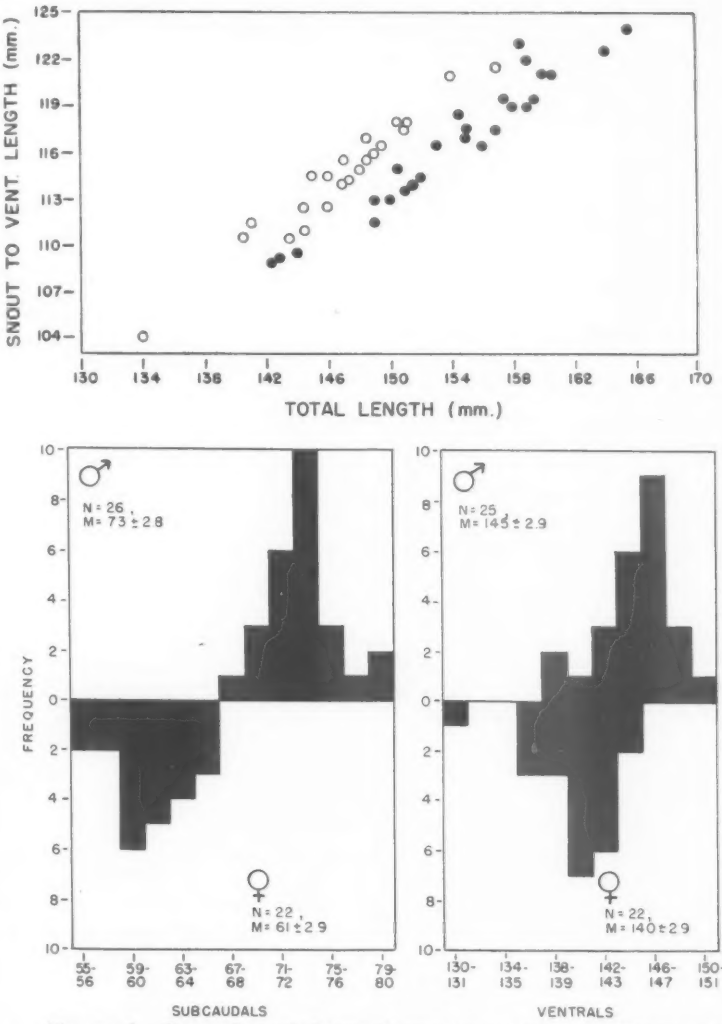

FIGURE 1.—Some Sexual Dimorphisms in a Brood of *Thamnophis o. ordinatus* (L.) from Warwick County, Virginia. (Above) Total lengths of 22 females (circles) and 26 males (spots) plotted against their snout-vent lengths. (*Below*) Subcaudal and ventral scute complements.

proportions that separates males from females regardless of length. This difference arises from the presence of a distinct sexual dimorphism in tail lengths, of the magnitude reported by Burt (1927) for adult specimens. The sexual differences in tail length are present throughout the lives of these snakes, and are not acquired with the attainment of maturity.

Variations in scutellation paralled differences in proportion. Like the total lengths, the ventral scute complements occupied overlapping ranges, while showing distinct differences in their means. Males had from 138 to 150 ventrals, averaging 145±2.9; females had from 131 to 144, averaging 140±2.9. Only 25 males were studied for this count because the remaining specimen had abnormal (double-row) ventral scutellation in some areas. This incomplete sexual dimorphism in ventral complements (figure 1, lower right) is distinctly different from the complete dimorphism in subcaudal complements (figure 1, lower left). The subcaudal complements, paralleling differences in tail lengths, occupied discrete ranges. Males had from 67 to 80 subcaudals, averaging 73±2.8; females had from 55 to 66, averaging 61±2.9.

Cephalic scutellation was studied on the right and left sides of the head of every specimen. No sexual dimorphism connected with cephalic scutellation was detected. Supralabials, infralabials, and oculars were quite consistent in number, usually 7, 10, and 1-3 respectively. Four per cent of the specimens had 8 supralabials on one side, 9 infralabials on one side, or (in 9 per cent of the cases) either 2 or 4 postoculars. Temporals were variable in arrangement and number: 1-2-3 (50%); 1-2-2 (15%); 1-3 (13%); 1-2 (10%); 1-1-3 (4%); 1-2-4 (4%); 1-3-2 (2%); 1-3-3 (2%). Lack of bilateral symmetry in head scutellation was common.

DISCUSSION

At time of birth the mean total lengths and ventral complements of male *Thamnophis o. ordinatus* (L.) exceed those of females, but extensively overlapped ranges make these measurements useless in distinguishing between the sexes. In this series of specimens subcaudal complements and tail length percentages of total length are discrete sexual dimorphisms.

Differences in subcaudal complements of the Common Garter Snakes in Virginia, Maryland, and Ohio were neither marked nor consistent, and would not serve to distinguish between specimens from these regions; in this regard ventral complements are of more interest, as follows:

VENTRAL SCUTE COMPLEMENTS

	MALES	FEMALES
VIRGINIA	138-150;	131-144;
(Coastal plain)	av. 145	av. 140
MARYLAND	142-159;	135-151;
(McCauley, 1945)	av. 149	av. 143
OHIO	145-160;	142-158;
(Conant, 1939)	av. 154	av. 149

If the scutellation of Common Garter Snakes of the Virginia Coastal Plain parallels the scale counts of the 48 specimens from a brood from that area which was studied in this report, the marked differences indicated by ventral complements may serve to determine the presence of distinct races in these areas.

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The River Shrimp, *Macrobrachium ohione* (Smith), in Virginia[1]

HORTON H. HOBBS, JR. AND WILLIAM H. MASSMANN
University of Virginia and Virginia Fisheries Laboratory

The "river shrimp" belonging to the genus *Macrobrachium*, which range in length from 34 to more than 230 mm., are not to be confused with the smaller "glass shrimp" belonging to the genus *Palaemonetes*, at least one species of which is a common form in the waters of the Piedmont and Coastal Plain of Virginia.

Hedgpeth[2] has recently summarized and added to the available data on the ecological and geographic distribution of the four species of the genus *Macrobrachium* found in the United States. In this work he includes diagnoses, figures, and a key to the species occurring north of the Rio Grande River.

The range of *Macrobrachium ohione* (Smith), the only endemic member of the genus in North America, and the most widespread form in the United States, was previously known to extend from Avoca, Bertie County, North Carolina (Albemarle Sound) to Aransas Bay, Texas, and northward in the Mississippi drainage system to Illinois and Ohio.

During the course of faunistic studies by the junior author in the tidal portions of the streams emptying into the lower Chesapeake, a single female specimen of *M. ohione* was collected from the James River at Hopewell on April 16, 1952[3]. The specimen was taken in a one meter hoop net of nylon marquisette (about 25 meshes per inch) which was anchored on the bottom in 15 feet of water where it was left for about 80 minutes.

In more than 2000 samples (including a number made with minnow seines) taken during the spring months, 1949-1952, from brackish water (salinity five parts per thousand) to the head of the tidewaters in the James, Appomattox, Chickahominy, Pamunkey, Mattaponi, and Rappahannock rivers this is the only specimen of *Macrobrachium* taken. Since it is known that this species invades salt water it is possible that *M. ohione* frequents most of the streams flowing into the Chesapeake Bay.

Although *M. ohione* is of economic importance in Louisiana as an

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1 Contribution from the Virginia Fisheries Laboratory, No. 40, and the Miller School of Biology.

2 Hedgpeth, J. W. (1949) The North American Species of Macrobrachium (River Shrimp). Texas Jour. Sci., 1 (3): 28-38, 5 figs.

3 This specimen has been deposited in the collection of the United States National Museum.

item of food, its apparent rarity in Virginia waters would seem to preclude a corresponding value placed on it here. Nonetheless, it should be pointed out that no attempt has been made to trap this shrimp in a manner in which it is taken in numbers elsewhere.

NEWS AND NOTES

SECTION NEWS

AGRICULTURAL SECTION

Dr. P. H. Massey has been appointed Associate Professor of Vegetable Crops in the Department of Horticulture at Virginia Polytechnic Institute. Dr. Massey is a native of North Carolina where he received his Bachelor's and Master's degrees. His Ph.D. work was done at Cornell University where he received the degree in February 1952.

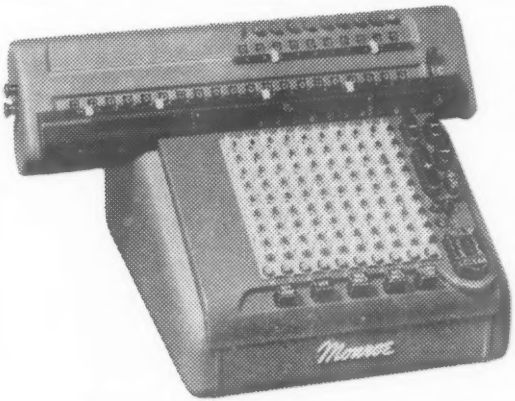
Mr. George Williams has been appointed Associate Extension Specialist in Vegetable Crops at Virginia Polytechnic Institute. Mr. Williams is a native of Texas where he took his undergraduate work. He received a Master's degree from Virginia Polytechnic Institute in June 1951 and until his appointment as Extension Vegetable Specialist was Assistant County agent in Roanoke County, Virginia.

Dr. Maynard G. Hale has been appointed Associate Plant Physiologist in the Department of Plant Pathology and Physiology, Virginia Polytechnic Institute, to replace Dr. John I. Shafer who resigned July 1, 1951, to enter private business. Dr. Hale received the B. S. Degree in agriculture in 1947, M. S. in 1949, and Ph.D. in 1951 at the Ohio State University. His duties which began on September 1, 1951 are divided between teaching elementary and advanced plant physiology and doing research. Dr. Hale's main interests are general plant physiology, plant growth, and the physiology of disease resistance.

Denver Bragg has completed assembling the thesis material for his M. S. degree at Virginia Polytechnic Institute and has submitted the summary for publication. The topic of his work is "An Attempt to Determine the Cause of Curled or Deformed Tongues in Young Beltsville White Turkeys."

Dr. Daniel L. Hallock, a native of Wisconsin, who received his doctorate at the University of Wisconsin in Soils will join the staff of the Agronomy Department, Virginia Polytechnic Institute about June 1, 1952, for the purpose of doing soil research work at the Tidewater Field Station at Holland, Virginia.

Some recent changes in the Animal Husbandry Department at Virginia Polytechnic Institute are K. C. Williamson, former Assistant County Agent in Halifax and Pittsylvania, has replaced M. L. Dalton, Agricultural Livestock Marketing Specialist of the Animal Husbandry Department. Mr. Hugh E. Henderson, former County Agent of Clark County, Virginia, replaced D. E. Brower, 4-H Club Specialist of the Animal Husbandry Department, and George A. Allen, Jr. former County Agent of Grayson County, has replaced George W. Litton as



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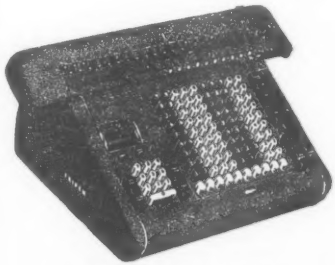

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Sheep Specialist. All this has taken place since January 1.

Mr. Dalton and Mr. Brower have gone to work for private concerns in the beef cattle business. A resignation from the Animal Husbandry Department as of February 15 was A. T. Lassiter, Jr., Swine Marketing Specialist, who has not been replaced as yet.

Paul W. Stoneburner, Assistant Agricultural Engineer, Virginia Polytechnic Institute Agricultural Experiment Station has resigned, effective May 31, 1952, to accept a position with a commercial concern in Virginia at a greatly increased compensation. Mr. Stoneburner has working on a cooperative project with the Engineering Experiment Station on "Nailed Trussed Rafters." He is co-author with Professor Stern of the Wood Research Laboratory, of the bulletin entitled, "Nailed Structural Joints Reinforced With Toothed-Ring Fasteners."

H. W. Glover, formerly Assistant Agricultural Engineer, Rural Housing, Agricultural Experiment Station, was transferred to the Agricultural Extension Division, May 1. He will have charge of the Farm Building Plan Service of the Agricultural Engineering Department.

Mr. Mark H. Kirkpatrick, Jr., Agricultural Engineer, SCS Research, Agricultural Engineering Department, Virginia Polytechnic Institute resigned March 10, 1952, to join the Sales Engineering Staff of the International Harvester Company at Greensboro, North Carolina. Mr. Kirkpatrick was engaged in agricultural hydrologic analyses and is co-author with Mr. H. N. Holtan of a series of technical papers concerned with the development of new methods of runoff computation through use of rainfall, infiltration and hydraulics of flow factors.

—WESLEY P. JUDKINS, *Virginia Agricultural Experiment Station, Blacksburg.*

BIOLOGY SECTION

At the annual meeting of the Biology Section, May 16, 1952, Mr. Robert T. Brumfield, Professor of Biology, Longwood College was elected to the editorial board of the Virginia Journal of Science. Items for publication in this section of the Journal should in the future be sent directly to him.

A New Journal in Zoology.—The first issue of a quarterly journal, Systematic Zoology, appeared in March. In this and future numbers articles of general interest to all zoological systematists will occupy most of the space in the journal; however, book notices, news items, projects, museum activities, and lists of systematic societies will be included. Occupying a hitherto conspicuous void in the coverage of zoological fields by scientific journals, the new serial has three purposes: "(1) to publish, and therefore to encourage the preparation of, contributions on basic aspects of all fields of systematic principles and problems: (2) to provide a suitable forum for discussion of the problems of the systematist and his methods; and (3) to report the other activi-

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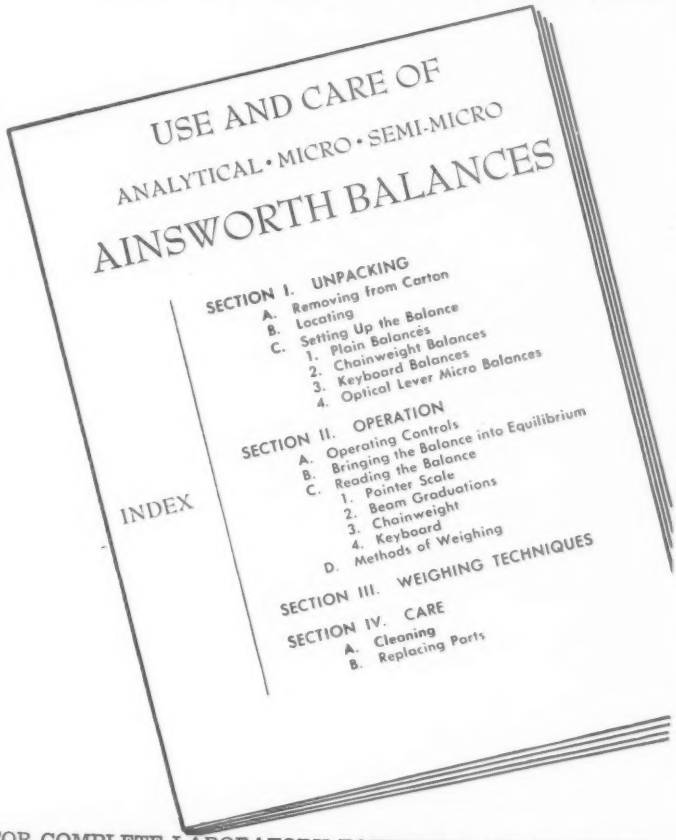

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ties of the Society of Systematic Zoology as news." Correspondence regarding subscriptions and membership should be addressed to the secretary of the Society, Dr. R. E. Blackwelder, Room 429, United States National Museum, Washington 25, D. C.

—LADLEY HUSTED, *University of Virginia.*

CHEMISTRY SECTION

A seminar on "The Conduct of Research and Development," held by the Virginia-Carolina Chemical Corporation, in Richmond, on April 25, was attended by about one hundred members of the Corporation and about fifty guests from the Virginia Section of the American Chemical Society. Following divisional meetings in the morning, a panel of speakers, with Dr. S. S. Negus, of the Medical College of Virginia, as moderator, included Dr. Allan T. Gwathmey, Research Professor at the University of Virginia and President of the Virginia Institute of Scientific Research, "Fundamental Research, Our Seedbed"; Dr. Lauren B. Hitchcock, President of National Dairy Research Laboratories, Oakdale, Long Island, "Applied Research and Development"; Dr. Milton Harris, President of Harris Research Laboratories, Washington, D. C., "Research and Development—Who, When, Where, and How"; and Dr. John Weiss, Chemical Engineer, New City, "Evaluation of Research and Development Projects". In the evening, a joint meeting of the Corporation and the Virginia Section was addressed by former governor of the Commonwealth, Hon. Colgate W. Darden, now President of the University of Virginia, on "Scientific Research and Our American Way of Life."

The designation "James Lewis Howe Awards" was chosen by the Blue Ridge Section, A. C. S., for the gifts of student affiliateship to one student from each of the ten schools in their territory that offer the bachelor's degree with a major in chemistry or in chemical engineering.

The Research Corporation has awarded $3200 to Dr. Thomas C. Franklin, Assistant Professor of Physical Chemistry at the University of Richmond, for the study of adsorption on the hydrogen electrode. Mr. Ray B. Southern, graduate student in chemistry, will assist with the project.

Publications from the University of Richmond: "Tris-(hydroxymethyl)-aminomethane Derivatives. II. Alkylation Products," J. Stanton Pierce and John Wotiz, *Journal of the American Chemical Society*, 73, 2594 (1951); "III. Oxamides, Ureas, Oxazolidines and 1-Aza-3, 7-dioxabicyclo (3.3.0) octanes," J. Stanton Pierce, Carl D. Lunsford, R. W. Raiford, Jr., J. L. Rush, and Douglas W. Wiley, *ibid.*, 73, 2595 (1951); "IV. Substituted 4-Hydroxymethyloxazolidines; Ester and Amide Interchange," J. Stanton Pierce and Carl D. Lunsford, *ibid.*, 73, 2596 (1951). "2-Methyl-2-monoalkylaminopropyl and Dialkylaminoethyl Aryloxyacetates," J. Stanton Pierce, William K.

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Easley and H. H. Hannabas, Jr., *ibid.*, 73, 4046 (1951).

Dr. Harvey B. Haag, Professor of Pharmacology at the Medical College of Virginia, was selected as President-Elect of the American Society for Pharmacology and Experimental Therapeutics at its forty-second meeting held in New York City. Doctor Haag was secretary of this organization from 1947 to 1951. Only once before has its presidency been held by a scientist from a southern institution.

Dr. John Baxter, of Washington and Lee University, will spend his second summer at the Oak Ridge National Laboratories.

Miss Jane Maxwell, of Sweetbrier College, has been awarded a fellowship for study this summer at Emory University.

Ten members of the Student Affiliate Chapter, A. C. S., of the Virginia Military Institute attended the national meeting of the Society in Milwaukee, Wisconsin, in April. They were Cadets Braswell, Cox, Crosswhite, Gottwald, Kallelis, Kulme, Mitchell, Radowski, Shorter, and Trigg. —WILLIAM E. TROUT, *University of Richmond*

ENGINEERING SECTION

At the Second Midwestern Conference on Fluid Mechanics at Ohio State University, Columbus, Ohio, March 17-19, 1952, two papers were presented by members of the Engineering Section:

"A New Expression for the Pressure Coefficient for Two-Dimensional Supersonic Flow" by R. W. Truitt, Virginia Polytechnic Institute, Blacksburg, Virginia. and

"Slamming of Ships" by V. G. Szebehely, David Taylor Model Basin, Navy Department, Washington, D. C.

—N. F. MURPHY, *Virginia Polytechnic Institute.*

SECTION OF SCIENCE TEACHERS

Johnson Addresses First Conference For Teachers Of Science

On April 25, the University of Virginia held its first Conference for Teachers of Science. Dr. Phillip G. Johnson, Science Specialist, U. S. Office of Education, was the featured speaker. Dr. Johnson spoke on "Emphasizing Scientific Methods in Science Teaching." Teachers from secondary schools, private schools, and colleges throughout Virginia attended this Conference.

Following the address, discussion groups were held. Dr. Ladley Husted, Professor of Biology, University of Virginia, served as leader for the group interested in teaching of the biological sciences. The group interested in the teaching of the physical sciences was led by Dr. James Cole, Professor of Chemistry, University of Virginia. Mr. F. G. Kizer, President of the Science Section of the Virginia Education Association, led the discussion on the teaching of general science.

The afternoon was devoted to departmental visitation. At this time members of the Conference had the opportunity of visiting the

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Biology, Chemistry, Physics, and Engineering Departments of the University of Virginia. During these visits teachers had the opportunity to observe student projects and laboratory demonstrations and conferred with members of the faculties concerning specific problems of interest.

This conference was the first of an annual series of conferences for teachers of science. The second will be held in the Spring of 1953 at the University of Virginia. —L. W. JARMAN, *Richmond, Virginia.*

STATISTICS SECTION

R. A. Bradley and M. E. Terry of the Department of Statistics and Statistical Laboratory, Virginia Polytechnic Institute, placed second in the competition for the J. Shelton Horsley Research Award sponsored by the Virginia Academy of Science. The joint papers presented in this competition are entitled "Rank Analysis of Incomplete Block Designs—The Method of Paired Comparisons" and "New Designs and Techniques in Organoleptic Testing." This research is part of a current project sponsored by the United States Department of Agriculture.

Boyd Harshbarger will serve as Chairman of the session on Experimental Design at the Gordon Research Conference on Statistics in Chemistry on July 29 at New Hampton, New Hampshire.

Boyd Harshbarger, R. A. Bradley, D. B. Duncan, M. E. Terry,

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and T. S. Russell, of the Department of Statistics and Statistical Laboratory, Virginia Polytechnic Institute, attended the meetings of the Blue Ridge Conference at Blue Ridge, North Carolina, during June and July. Drs. Bradley and Terry presented an invited address. Dr. Harshbarger led a discussion on research in statistics.

—M. E. TERRY, *Virginia Polytechnic Institute.*